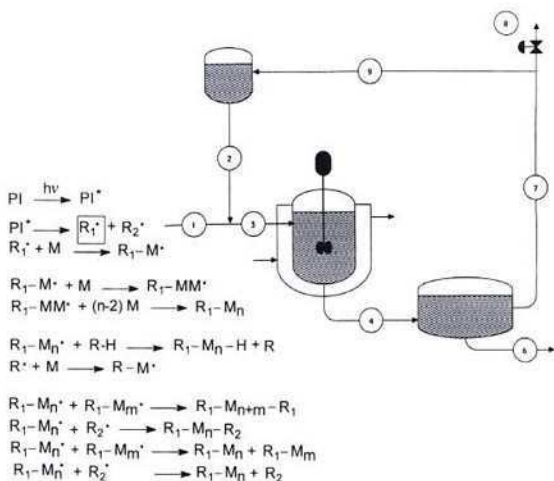


HANDBOOK OF RADICAL VINYL POLYMERIZATION



MUNMAYA K. MISHRA
YUSUF YAGCI

HANDBOOK OF RADICAL VINYL POLYMERIZATION

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PRINTED IN THE UNITED STATES OF AMERICA

To my parents and my wife, Bidu—MKM

To my wife, Emine—YY

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Preface

The field of vinyl polymerization has grown very large indeed. The momentum of extensive investigations on radical vinyl polymerization, undertaken in many laboratories, has carried us to an advanced stage of development. Consequently, we are attempting in this *Handbook of Radical Vinyl Polymerization* to present current knowledge of the subject in an integrated package.

The book is primarily concerned with the physical and organic chemistry of radical vinyl polymerization, with special emphasis on initiators and mechanisms. The first three chapters provide the fundamental aspects. The most important and interesting feature of the book is in the following chapters, which offer a detailed description of the radical initiating systems and mechanisms, along with the technical processes. Another chapter throws light on living polymerization, one of the recent advances in the field. The book ends with a chapter that presents a variety of data on monomers and polymerization.

It is hoped that this presentation will prove useful to investigators in the area of radical vinyl polymerization. The book offers much that is of value, presenting basic information in addition to providing a unified, interlocking, and in many respects new view of radical vinyl polymerization. Although selected parts of this discipline have been reviewed in the past, this is the first time that the whole field has been comprehensively and critically examined in a book. However, it would scarcely be possible in a single volume to do justice to all the excellent research in various branches of the subject; selection of the material to be included was difficult and an element of arbitrariness was unavoidable.

This is an interdisciplinary book written for the organic chemist/polymer scientist who wants comprehensive, up-to-date critical information

about radical vinyl polymerization and technology and for the industrial researcher who wants to survey the technology of radical polymerization processes leading to useful products.

Specifically, this book will serve in the following ways: (1) as a reference book for researchers in radical polymerization, (2) as a coherent picture of the field and a self-educating introductory and advanced text for the practicing chemist who has little background in radical polymerization, (3) as one of a group of textbooks for courses in the graduate-level curriculum devoted to polymer science and engineering.

It would not have been possible to complete a project like this without the help and participation of numerous individuals. We gratefully acknowledge all the contributors who made this book possible. Our sincere thanks go to Prof. Kyu Yong Choi and his team, who contributed the two chapters that constitute Part III, Technical Processes of Vinyl Polymerization, an important part of this book. Without his contribution the book would have been incomplete—his expertise and contributions made this possible. We would like to thank Dr. Aysen Onen and Yesim Hepuzer for providing valuable references and chemical drawings during the preparation of various chapters of this book.

I (MKM) would like to extend my sincere thanks to Prof. P. L. Nayak and Prof. S. Lenka whose association made possible my entry into the area of radical vinyl polymerization in the late 1970s. Undoubtedly that entry gave me the opportunity today to design a book in this field. I also wish to thank my parents for their support and encouragement.

Last, with love and appreciation we acknowledge our wives Bidulata Mishra and Emine Yagci for their timely encouragement, sacrifice, and support during long afternoons, weekends, early mornings, and holidays spent on this book. Without their help and support this project would never have started or been completed.

Munmaya K. Mishra
Yusuf Yagci

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I

THE FUNDAMENTALS

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1

Introduction

Yusuf Yagci and Munmaya K. Mishra

I. WHAT ARE RADICALS?

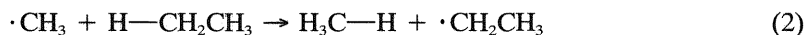
Organic molecules containing an unpaired electron are termed free radicals or radicals, and radicals are generally considered to be unstable species because of their very short lifetimes in the liquid and gaseous state. The instability of free radicals is a kinetic rather than a thermodynamic property.

Free radicals can undergo four general types of reactions: (1) transfer or abstraction, (2) elimination, (3) addition, and (4) combination or coupling. These reactions can be illustrated by the following example [1]. The pyrolysis of ethane in the gas phase is a free-radical reaction and the products are formed from the initial homolytic decomposition.

Decomposition:



Transfer/Abstraction Reaction (hydrogen-atom transfer reaction between methyl radical and ethane):

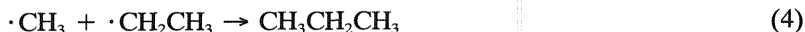


Elimination Reaction (elimination of hydrogen atom from the ethyl radical):



(better known as disproportionation reaction)

Combination Reaction (formation of propane by combination of methyl and ethyl radicals):



Addition Reaction (addition of methyl radicals to ethylene to form propyl radicals):



These four basic types of reaction account for the mechanism and products of free-radical polymerization.

II. HOW RADICALS ARE GENERATED?

Virtually all free-radical chain reactions require a separate initiation step in which a radical species is generated in the reaction mixture or by adding a stable free radical (generated by a separate initiation step) directly to the reactants. Radical initiation reactions, therefore, can be divided into two general types according to the manner in which the first radical species is formed; these are (1) homolytic decomposition of covalent bonds by energy absorption or (2) electron transfer from ions or atoms containing unpaired electrons followed by bond dissociation in the acceptor molecule.

A. Homolytic Decomposition of Covalent Bonds

Organic compounds may decompose into two or more free-radical fragments by energy absorption. The energy includes almost any form, including thermal, electromagnetic (ultraviolet and high-energy radiation), particulate, electrical, sonic, and mechanical. The most important of these are the thermal and electromagnetic energies. For the generation of free radicals by energetic cleavage, the important parameter is the bond dissociation energy, D . The bond dissociation energy is the energy required to break a particular bond in a particular molecule. The bond dissociation energy can be used to calculate the approximate rate of free-radical formation at various temperatures according to the following reaction:



$$\frac{d[\text{R}\cdot]}{dt} = k[\text{R}_2] \quad (7)$$

$$k = Ae^{-D/RT} \quad (8)$$

Pure thermal dissociation is generally an unimolecular reaction and D is very close to the activation energy, ΔE^\ddagger . For an unimolecular reaction [1], the frequency factor, A , is generally of the order 10^{13} – 10^{14} sec^{-1} . Most practical thermal initiators are compounds with bond dissociation energies in the range of 30–40 kcal mol^{-1} . This range of dissociation energies limits the types of useful compound to those containing fairly specific types of covalent bonds, notably oxygen–oxygen bonds, oxygen–nitrogen bonds, and sulfur–sulfur bonds, as well as unique bonds present in azo compounds.

Table 1 Polymerizability of Monomers by Different Polymerization Mechanisms

Monomer	Types of polymerization		
	Radical	Cationic	Anionic
Acrylonitrile	Yes	No	Yes
Acrylamide	Yes	No	No
1-Alkyl olefins	No	Yes	No
Acrylates	Yes	No	Yes
Aldehydes	No	Yes	Yes
Butene-1	No	No	No
Butadiene-1,3	Yes	Yes	Yes
1,1-Dialkyl olefins	No	Yes	No
1,3-Dienes	Yes	Yes	Yes
Ethylene	Yes	No	Yes
Halogenated olefins	Yes	No	No
Isoprene	Yes	Yes	Yes
Isobutene	No	Yes	No
Ketones	No	Yes	Yes
Methacrylic esters	Yes	No	Yes
Methacrylamide	Yes	No	Yes
Methacrylonitrile	Yes	No	Yes
Methyl styrene	Yes	Yes	Yes
Styrene	Yes	Yes	Yes
Tetrafluoroethylene	Yes	No	No
Vinyl chloride	Yes	No	No
Vinyl fluoride	Yes	No	No
Vinyl ethers	No	Yes	No
Vinyl esters	Yes	No	No
Vinylidene chloride	Yes	No	Yes
N-Vinyl carbazole	Yes	Yes	No
N-Vinyl pyrrolidone	Yes	Yes	No

III. COMPARISON OF FREE-RADICAL AND IONIC OLEFIN POLYMERIZATION REACTIONS

There are many fundamental differences in the mechanism of free radical compared to ionic chain-growth polymerization. The differences involve not only the rate and manner of polymer chain growth for each type of poly-

Table 2 Comparison of Free-Radical and Ionic Olefin Polymerization

Free Radical

1. End groups in growing polymer chains are truly free species.
2. It is generally felt that solvent polarity exerts no influence on free-radical propagation.
3. Radical polymerization reaction shows both combination and disproportionation termination reaction steps involve two growing polymer chains.
4. Termination reactions are bimolecular.
5. Due to the high rate of bimolecular termination, the concentration of growing polymer chains must be maintained at a very low level, in order to prepare high-molecular-weight polymer.
6. Radical polymerizations are versatile and can be initiated effectively in gas, solid, and liquid phases. Polymerizations can be carried out in bulk, solution, precipitation, suspension, and emulsion techniques. Each process has its own merits and special characteristics.

Ionic

1. End groups always have counterions, more or less associated.
 2. The association of the counterions, their stability, and the ionic propagation depend on the polarity of the medium.
 3. In cationic polymerization reaction, combination and disproportionation reactions occur between the end groups and the counterion of an active polymer chain (anion capture and proton release).
 4. Termination reactions are unimolecular.
 5. In ionic polymerization, a much higher concentration of growing polymer chains may be maintained without penalty to the molecular weights produced. In ionic polymerization, there is no tendency for two polymer chain end groups of like ionic charge to react. Due to much higher concentration of growing polymer chains in homogeneous polymerization reaction, the rates of ionic polymerization can be many times higher than that of a free-radical polymerization of the same monomer, even though the activation energies for propagation are comparable.
 6. Ionic polymerization is limited experimentally almost entirely to solution or bulk methods, although crystalline, solid-state polymerization is observed in some cases.
-

merization but also the selection of monomers suitable for each type of polymerization. The variety of behaviors can be seen in Tables 1 and 2.

REFERENCE

1. H. E. de la Mare and W. E. Vaughan, *J. Chem. Ed.*, **34**, 10 (1951).

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Chemistry and Kinetic Model of Radical Vinyl Polymerization

Yusuf Yagci and Munmaya K. Mishra

I. CHEMISTRY

Radical vinyl polymerization is a chain reaction that consists of a sequence of three steps: initiation, propagation, and termination.

A. Chain Initiation

The chain initiation step involves two reactions. In the first step, a radical is produced by any one of a number of reactions. The most common is the homolytic decomposition of an initiator species I to yield a pair of initiator or primary radicals R^\cdot :



where k_d is the rate constant for the catalyst dissociation.

The second step involves the addition of this radical R^\cdot to the first monomer molecule (M) to produce the chain-initiating species M_1^\cdot :



where k_i is the rate constant for the second initiation step.

B. Chain Propagation

Propagation consists of the growth of M_1^\cdot by the successive addition of large number of monomer molecules (M). The addition steps may be represented as follows:



etc. In general, the steps may be represented as



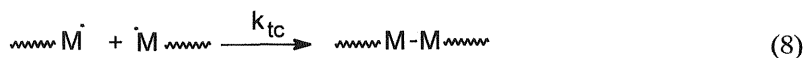
where k_p is the propagation rate constant.

C. Chain Termination

Chain propagation to a high-molecular-weight polymer takes place very rapidly. At some point, the propagating polymer chain stops growing and terminates. Termination may occur by various modes as follows.

Combination (coupling):

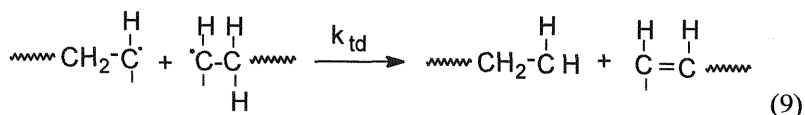
Two propagating radicals react with each other by combination (coupling) to form a dead polymer:



where k_{tc} is the rate constant for termination by coupling.

Disproportionation:

This step involves a hydrogen radical that is beta to one radical center transferred to another radical center to form two dead polymer chains (one saturated and one unsaturated):

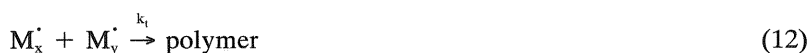


where k_{td} is the rate constant for termination by disproportionation.

Termination can also occur by a combination of coupling and disproportionation. The two different types of termination may be represented as follows:



In general, the termination step may be represented by the



II. KINETIC MODEL (RATE EXPRESSIONS)

By considering Eq. (1), the rate of decomposition, R_d , of the initiator (I) may be expressed by the following equation in which k_d is the decay or rate constant:

$$R_d = -\frac{d[I]}{dt} = k_d[I] \quad (13)$$

Similarly, by considering Eq. (2), the rate of initiation, R_i , may be expressed as follows, where k_i is the rate constant for the initiation step:

$$R_i = \frac{d[M_i^\cdot]}{dt} = k_i[R^\cdot][M] \quad (14)$$

The rate of initiation, which is the rate-controlling step in free-radical polymerization, is also related to the efficiency of the production of two radicals from each molecule of initiator, as shown in the following rate equation:

$$R_i = 2k_d f[I] \quad (15)$$

Propagation is a bimolecular reaction which takes place by the addition of the free radical to another molecule of monomer, and by many repetitions of this step as represented in Eqs. (3)–(7). The propagation rate constant k_p is generally considered to be independent of the chain length.

The rate of monomer consumption ($-d[M]/dt$), which is synonymous with the rate of polymerization (R_p), may be defined as

$$-\frac{d[M]}{dt} = R_p = k_p[M_n^\cdot][M] + k_i[R^\cdot][M] \quad (16)$$

For long chains, the term $k_i[R'] [M]$ may be negligible, as the amount of monomer consumed by the initiation step [Eq. (2)] is very small compared with that consumed in propagation steps. The equation for R_p may be re-written as

$$R_p = k_p[M_n'] [M] \quad (17)$$

The termination of the growing free-radical chains usually takes place by coupling of two macroradicals. Thus, the kinetic chain length (ν) is equal to the half of degree of polymerization, $DP/2$. The reaction for the bimolecular termination is presented in Eq. (8). The kinetic equation for termination by coupling is

$$R_t = -\frac{d[M']}{dt} = 2k_t[M']^2 \quad (18)$$

Termination of free-radical chain polymerization may also take place by disproportionation. The description for chain termination by disproportionation is given in Eq. (9). The kinetic chain length (ν) is the number of monomer molecules consumed by each primary radical and is equal to the rate of propagation divided by the rate of initiation for termination by disproportionation. The kinetic equation for the termination by disproportionation is

$$R_{td} = 2k_{td}[M']^2 \quad (19)$$

The equation for the kinetic chain length for termination by disproportionation may be represented as

$$\nu_t = \frac{R_p}{R_i} = \frac{R_p}{R_{td}} = \frac{k_p[M][M']}{2k_{td}[M']^2} = \frac{k_p[M]}{2k_{td}[M']} = DP = \frac{k''[M]}{[M']} \quad (20)$$

The rate of monomer–radical change can be described as the monomer–radical formed minus (monomer radical utilized), that is

$$\frac{d[M']}{dt} = k_i[R'] [M] - 2k_t[M']^2 \quad (21)$$

It is experimentally found that the number of growing chains is approximately constant over a large extent of reaction. Assuming a “steady-state” condition, $d[M']/dt = 0$, and

$$k_i[R'] [M] = 2k_t[M']^2 \quad (22)$$

$[M']$ can be derived by solving Eq. (22):

$$[M'] = \left(\frac{k_i[R'][M]}{2k_t} \right)^{1/2} \quad (23)$$

Similarly, assuming a "steady-state" condition for the concentration of R' and taking into consideration Eqs. (14) and (15), the following equation may be derived:

$$\frac{d[R']}{dt} = 2k_d f[I] - k_i[R'][M] = 0 \quad (24)$$

Solving for $[R']$ from Eq. (24) gives

$$[R'] = \frac{2k_d f[I]}{k_i[M]} \quad (25)$$

Substituting $[R']$ into Eq. (23), the expression for $[M']$ can be represented as

$$[M'] = \left(\frac{k_d f[I]}{k_t} \right)^{1/2} \quad (26)$$

which contains readily determinable variables. Then, by using the relationship for $[M']$ as shown in Eqs. (17), (18), and (20), the equation for the rate of polymerization and kinetic chain length can be derived as follows:

$$R_p = k_p[M][M'] = k_p[M] \left(\frac{k_d f[I]}{k_t} \right)^{1/2} = [M][I]^{1/2} \left(\frac{k_p^2 k_d f}{k_t} \right)^{1/2} = k'[M][I]^{1/2} \quad (27)$$

where $k' = (k_p^2 k_d f / k_t)^{1/2}$,

$$R_t = 2k_t[M']^2 = \frac{2k_i k_d f[I]}{k_t} = 2k_d f[I] \quad (28)$$

$$\overline{DP} = \frac{R_p}{R_t} = \frac{k_p[M](k_d f[I]/k_t)^{1/2}}{2k_d f[I]} = \frac{k_p[M]}{2(k_d k_t f[I])^{1/2}} \quad (29)$$

$$\overline{DP} = \frac{M}{[I]^{1/2}} \frac{k_p}{(2k_d k_t f)^{1/2}} = \frac{M}{[I]^{1/2}} k'' \quad (30)$$

where $k'' = k_p / (2k_d k_t f)^{1/2}$.

III. CONCLUSIONS

The following conclusions may be made about free-radical vinyl polymerization using a chemical initiator:

- The rate of propagation is proportional to the concentration of the monomer and the square root of the concentration of the initiator.
- The rate of termination is proportional to the concentration of the initiator.
- The average molecular weight is proportional to the concentration of the monomer and inversely proportional to the square root of the concentration of the initiator.
- The first chain that is initiated rapidly produces a high-molecular-weight polymer.
- The monomer concentration decreases steadily throughout the reaction and approaches zero at the end.
- Increasing the temperature increases the concentration of free radicals and, thus, increases the rate of reactions, but decreases the average molecular weight.
- If the temperature exceeds the ceiling temperature (T_c), the polymer will decompose and no propagation will take place at temperatures above the ceiling temperature.

3

Special Characteristics of Radical Vinyl Polymerization

Yusuf Yagci and Munmaya K. Mishra

I. INITIATOR HALF-LIFE

Depending on the structure, various radical initiators decompose in different modes and the rates of decomposition are different. The differences in the decomposition rates of various initiators can be conveniently expressed in terms of the initiator half-life $t_{1/2}$, defined as the time for the concentration of I to decrease to one-half its original value.

II. INITIATOR EFFICIENCY

In radical polymerization, the initiator is inefficiently used due to various side reactions. Also, the amount of initiator that initiates the polymerization is always less than the amount of initiator that is decomposed during a polymerization. The side reactions are chain transfer to initiator (discussed later) (i.e., the induced decomposition of initiator by the attack of propa-

gating radicals on the initiator) and the radicals reactions to form neutral molecules instead of initiating polymerization.

The initiator efficiency (I_{eff}) is defined as the fraction of radicals formed in the primary step of initiator decomposition, which are successful in initiating polymerization.

III. INHIBITION AND RETARDATION

Certain substances, when added to the polymerization system, may react with the initiating and propagating radicals converting them either to non-radical species or to less reactive radicals to undergo propagation. Such additives are classified according to their effectiveness:

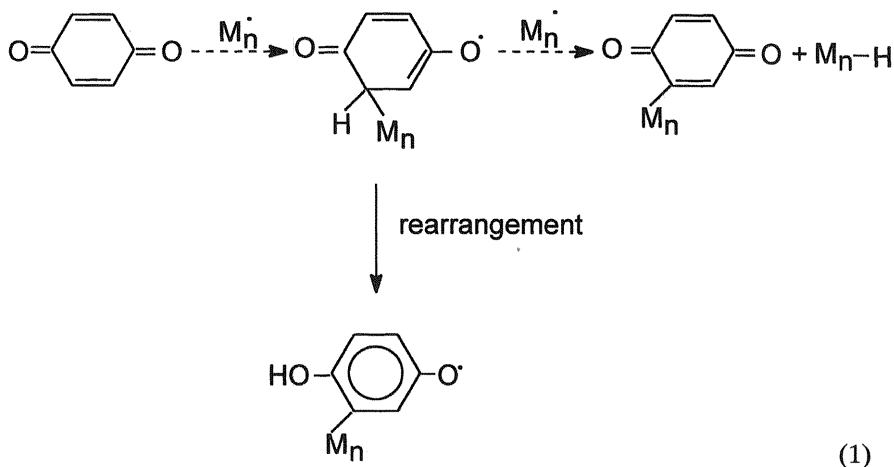
Inhibitors stop every radical, and polymerization is completely ceased until they are consumed.

Retarders, on the other hand, are less efficient and halt a portion of radicals. In this case, polymerization continues at a slower rate.

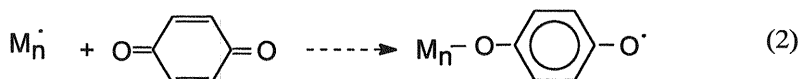
For example, in the case of thermal polymerization of styrene [1], benzoquinone acts as an inhibitor. When the inhibitor has been consumed, polymerization regains its momentum and proceeds at the same rate as in the absence of the inhibitor. Nitrobenzene [1] acts as a retarder and lowers the polymerization rate, whereas nitrosobenzene [1] behaves differently. Initially, nitrosobenzene acts as an inhibitor but is apparently converted to a product which acts as a retarder after the inhibition period. Impurities present in the monomer may act as inhibitors or retarders. The inhibitors in the commercial monomers (to prevent premature thermal polymerization during storage and shipment) are usually removed prior to polymerization or, alternatively, an appropriate excess of initiator may be used to compensate for their presence.

The useful class of inhibitors are molecules such as benzoquinone and chloranil (2,3,5,6-tetrachlorobenzoquinone) that react with chain radicals to yield radicals of low reactivity. The quinones behave very differently [2–5]. Depending on the attack of a propagating radical at the carbon or oxygen sites, quinone and ether are the two major products [5] formed, respectively. The mechanism may be represented as follows:

Attack on the ring carbon atom yields intermediate radical, which can undergo further reaction to form the quinone:



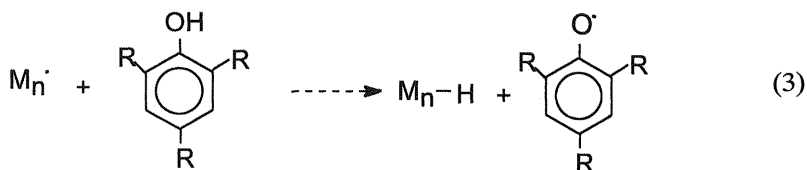
Attack of propagating radical at oxygen yields the ether type radical (aryloxy radical):



These preceding radicals, including the aryloxy radical, may undergo further reactions such as coupling or termination with other radicals.

The effect of quinones depend on the polarity of the propagating radicals. Thus, p-benzoquinone and chloranil (which are electron poor) act as inhibitors toward electron-rich propagating radicals (vinyl acetate and styrene) but only as retarders toward the electron-poor acrylonitrile and methyl methacrylate propagating radicals [6]. It is interesting to note that the inhibiting ability toward the electron-poor monomers can be increased by the addition of an electron-rich third component such as an amine (triethylamine).

Polyalkyl ring-substituted phenols, such as 2,4,6-trimethyl-phenol act as more powerful retarders than phenol toward vinyl acetate polymerization. The mechanism for retardation may involve hydrogen abstraction followed by coupling of the phenoxy radical with other polymer radicals:

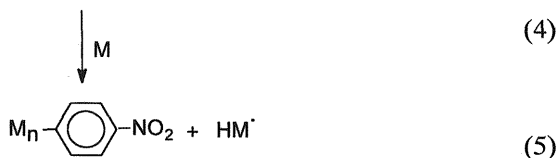
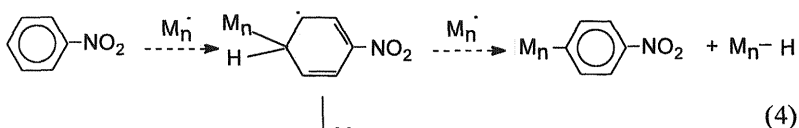


The presence of sufficient electron-donating alkyl groups facilitates the reaction.

Dihydroxybenzenes and trihydroxybenzenes such as 1,2-dihydroxy-4-t-butylbenzene, 1,2,3-trihydroxybenzene, and hydroquinone (p-dihydroxybenzene) act as inhibitors in the presence of oxygen [7,8]. The inhibiting effect of these compounds is produced by their oxidation to quinones [9].

Aromatic nitro compounds act as inhibitors and show greater tendency toward more reactive and electron-rich radicals. Nitro compounds have very little effect on methyl acrylate and methyl methacrylate [5,10,11] but inhibit vinyl acetate and retard styrene polymerization. The effectiveness increases with the number of nitro groups in the ring [12,13]. The mechanism of radical termination involves attack on both the aromatic ring and the nitro group. The reactions are represented as follows:

Attack on the ring:



Attack on the nitro group:

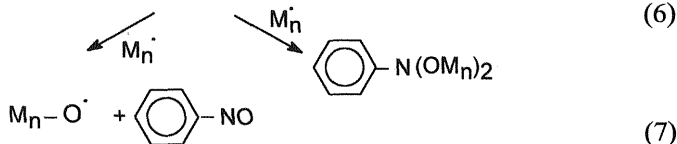
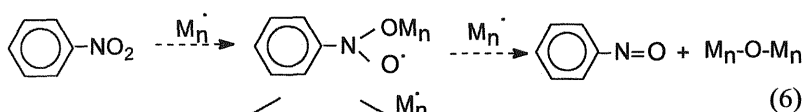
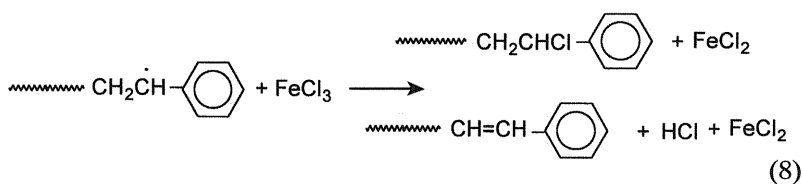


Table 1 Inhibitor Constants

Inhibitor	Monomer	Temp. (°C)	Constant (z)
Aniline	Methyl acrylate	50	0.0001
	Vinyl acetate	50	0.015
p-Benzoquinone	Acrylonitrile	50	0.91
	Methyl methacrylate	50	5.7
	Styrene	50	518.0
Chloranil	Methyl methacrylate	44	0.26
	Styrene	50	2,010
CuCl ₂	Acrylonitrile	60	100
	Methyl methacrylate	60	1,027
	Styrene	50	11,000
DPPH	Methyl methacrylate	44	2,000
p-Dihydroxybenzene	Vinyl acetate	50	0.7
FeCl ₃	Acrylonitrile	60	3.3
	Styrene	60	536
	Methyl acrylate	50	0.00464
Nitrobenzene	Styrene	50	0.326
	Vinyl acetate	50	11.2
Oxygen	Methyl methacrylate	50	33,000
	Styrene	50	14,600
Phenol	Methyl acrylate	50	0.0002
	Vinyl acetate	50	0.012
Sulfur	Methyl methacrylate	44	0.075
	Vinyl acetate	44	470
1,3,5-Trinitrobenzene	Methyl acrylate	50	0.204
	Styrene	50	64.2
	Vinyl acetate	50	404
1,2,3-Trihydroxybenzene	Vinyl acetate	50	5.0
2,4,6-Trimethylphenol	Vinyl acetate	50	5.0

where M and M_n are the monomer and the propagating radical, respectively.

Oxidants such as FeCl₃ and CuCl₂ are strong inhibitors [14–17]. The termination of growing radicals may be shown by the following reaction:



Oxygen is a powerful inhibitor. It reacts with radicals to form the relatively unreactive peroxy radical, which may undergo further reaction:



It may react with itself or another propagating radical to form inactive products [18–20]. It is interesting to note that oxygen is also an initiator in some cases. The inhibiting or initiating capabilities of oxygen are highly temperature dependent. Other inhibitors include chlorophosphins [21], sulfur, aromatic azo compounds [22], and carbon. The inhibitor constants of various inhibitors for different monomers are presented in Table 1.

IV. CHAIN TRANSFER

Chain transfer is a chain-stopping reaction. It results in a decrease in the size of the propagating polymer chain. This effect is due to the premature termination of a growing polymer chain by the transfer of a hydrogen or other atom from some compound present in the system (i.e., monomer, solvent, initiator, etc.). These radical displacement reactions are termed chain transfer reactions and may be presented as



where k_{tr} is the chain transfer rate constant, CTA is the chain transfer agent (may be initiator, solvent, monomer, or other substance), and C is the atom or species transferred. The rate of a chain transfer reaction may be given as

$$R_{tr} = k_{tr}[M \cdot][CTA] \quad (11)$$

The new radical $A \cdot$ which is generated by the chain transfer reaction may reinitiate polymerization:



The effect of chain transfer on the polymerization rate is dependent on whether the rate of reinitiation is comparable to that of the original propagating radical. Table 2 shows the different phenomena. The rate equation for the chain transfer reaction may be represented as (also known as the Mayo equation):

$$\frac{1}{X_n} = \frac{k_t R_p}{k_p''[M]''} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{k_t R_p''}{k_p'' f k_d [M]^3} \quad (13)$$

Table 2 Effect of Chain Transfer on R_p and X_n

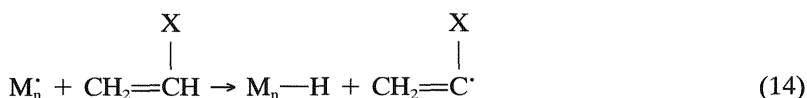
Rate constants ^a	Mode	Effect on R_p	Effect on X_n
1. $K_p \ll k_{tr}$ $k_a \sim k_p$	Telomerization	None	Large decrease
2. $K_p \gg k_{tr}$ $k_a \sim k_p$	Normal chain transfer	None	Decrease
3. $K_p \ll k_{tr}$ $k_a < k_p$	Degradative chain transfer	Large decrease	Large decrease
4. $K_p \gg k_{tr}$ $k_a < k_p$	Retardation	Decrease	Decrease

^a K_p , k_{tr} , and k_a are the rate constants for propagation, transfer, and reinitiation steps, respectively.

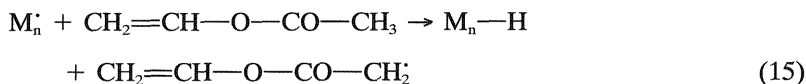
where X_n , R_p , k_t , C , S , and M are the degree of polymerization, rate of polymerization, termination rate constant, chain transfer constant, chain transfer agent, and monomer, respectively.

A. Chain Transfer to Monomer

The chain transfer constants of various monomers at 60°C are presented in Table 3. The monomer chain transfer constants C_M are generally small (10^{-5} – 10^{-4}) for most monomers because the reaction involves breaking the strong vinyl C–H bond:



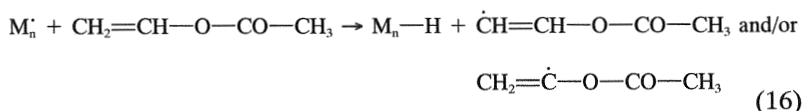
On the other hand, when the propagating radicals (polyvinyl acetate, ethylene, and vinyl chloride) have very high reactivity, the C_M is usually large. In the case of vinyl acetate polymerization [26], chain transfer to monomer has been generally attributed to transfer from the acetoxy methyl group:



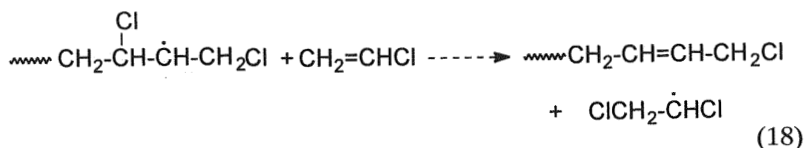
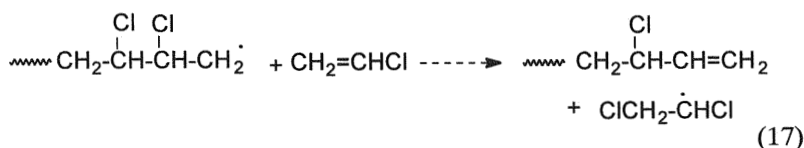
However, a different mechanism had been suggested by Litt and Chang [27]. By using vinyl trideuteroacetate and trideuterovinyl acetate, they indicated that more than 90% of the transfer occurs at the vinyl hydrogens:

Table 3 Chain Transfer Constants of Monomers

Monomer	$C_M \times 10^4$	Ref.
Acrylamide	0.6	12
Acrylonitrile	0.26–0.3	12
Ethylene	0.4–4.2	12
Methyl acrylate	0.036–0.325	12
Methyl methacrylate	0.07–0.25	12, 23
Styrene	0.30–0.60	24
Vinyl acetate	1.75–2.8	12
Vinyl chloride	10.8–16	12, 25



The very high value of C_M for vinyl chloride may be explained by the following reactions. It is believed [28] to occur by β -scission transfer of Cl to the monomer from the propagating center or, more likely, after that center undergoes intramolecular Cl migration [29]:



The C_M value of vinyl chloride is high enough that the number-average molecular weight that can be achieved is 50,000–120,000.

B. Chain Transfer to Initiator

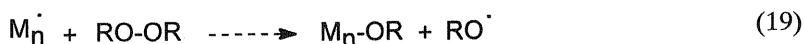
The transfer constants (C_I) for different initiators are presented in Table 4. The value of C_I for a particular initiator is dependent on the nature (i.e.,

Table 4 Initiator Chain Transfer Constant

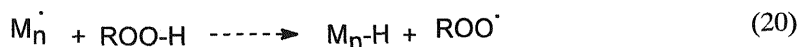
Initiator	Temp. (°C)	C _i for polymerization			Ref.
		STY ^a	MMA ^a	AM ^a	
2,2'-Azobisisobutyronitrile	60	0.091–0.14	0.02	—	23, 24
t-Butyl peroxide	60	0.00076–0.00092	—	—	12
t-Butyl hydroperoxide	60	0.035	—	—	12
Benzoyl peroxide	60	0.048–0.10	0.02	—	12
Cumyl peroxide	50	0.01	—	—	12
Cumyl hydroperoxide	60	0.063	0.33	—	12
Lauroyl peroxide	70	0.024	—	—	12
Persulfate	40	—	—	0.0026	30

^aSTY = styrene; MMA = methyl methacrylate; AM = acrylamide.

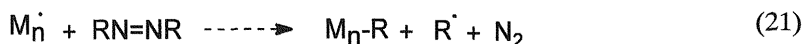
reactivity) of the propagating radical. For example, there is a very large difference in C_i for cumyl hydroperoxide toward the poly(methyl methacrylate) radical compared to the polystyryl radical. Peroxides usually have a significant chain transfer constant. The transfer reactions may be presented as follows:



where R is an alkyl or acyl group. The acyl peroxides have higher transfer constants than the alkyl peroxides due to the weaker bond of the former. The hydroperoxides are usually the strongest transfer agents among the initiators. The transfer reaction probably involves the hydrogen atom abstraction according to the following reaction:



The transfer reaction with azonitriles [23,24] probably occurs by the displacement reaction, which is presented as follows:



C. Chain Transfer to Chain Transfer Agent

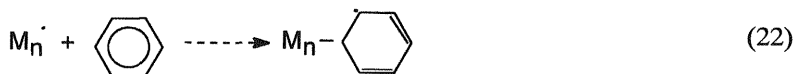
The chain transfer to the different substances other than the initiator and monomer (referred to as the chain transfer agent) is another special case. The example is the solvent or may be another added compound. The transfer constants for various compounds are shown in Table 5.

The transfer constant data presented in Table 5 may provide the information regarding the mechanism and the relationship between structure and reactivity in radical displacement reactions. For example, the low C_s values for benzene and cyclohexane are due to the strong C–H bonds present. It is interesting to note that transfer to benzene does not involve hydrogen abstraction but the addition of the propagating radical to the benzene ring [31] according to

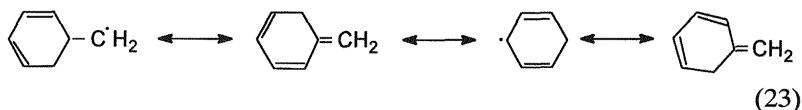
Table 5 Transfer Constants for Chain Transfer Agents

Transfer agent	$C_s \times 10^4$, polymerization at 60°C	
	Styrene	Vinyl acetate
Acetic acid	2.0	1.1
Acetone	4.1	11.7
Benzene	0.023	1.2
Butylamine	7.0	—
t-Butyl benzene	0.06	3.6
n-Butyl chloride	0.04	10
n-Butyl bromide	0.06	50
n-Butyl alcohol	1.6	20
n-Butyl iodide	1.85	800
n-Butyl mercaptan	210,000	480,000
Cyclohexane	0.031	7.0
2-Chlorobutane	1.2	—
Chloroform	3.4	150
Carbon tetrachloride	110	10,700
Carbon tetrabromide	22,000	390,000
Di-n-Butyl sulfide	22	260
Di-n-Butyl disulfide	24	10,000
Ethylbenzene	0.67	55.2
Ethyl ether	5.6	45.3
Heptane	0.42	17.0 (50°C)
Isopropylbenzene	0.82	89.9
Toluene	0.125	21.6
Triethylamine	7.1	370

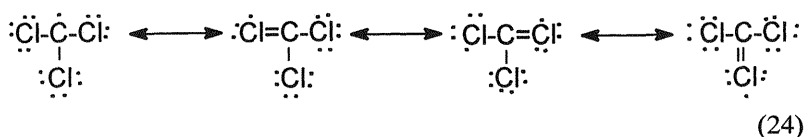
Source: Ref. 12.



The C_s values for toluene, isopropylbenzene, and ethylbenzene are higher than benzene. This is due to the presence of the weaker benzylic hydrogens and can be abstracted easily because of the resonance stability of the resultant radical:

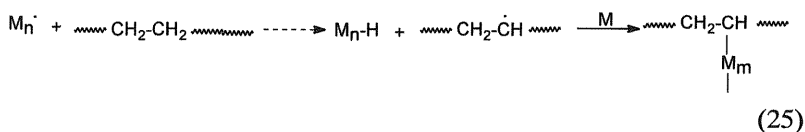


Primary halides such as n-butyl bromide and chlorine have low transfer constants like aliphatics. This may be explained by the low stability of a primary alkyl radical upon abstraction of Cl or Br. In contrast, n-butyl iodide shows a much higher C_s value, which transfers an iodide atom due to the weakness of the C–I bond. The high transfer constants for disulfides are due to the weak S–S bond. Amines, ethers, alcohols, acids, and carbonyl compounds have higher transfer constants than those of aliphatic hydrocarbons, due to the C–H bond breakage and stabilization of the radical by an adjacent O, N, or carbonyl group. The high C_s values for carbon tetrachloride and carbon tetrabromide are due to the weak carbon–halogen bonds. These bonds are especially weak because of the resonance stabilization of the resultant trihalocarbon radicals formed by the halogen abstraction:



D. Chain Transfer to Polymer

Chain transfer to polymer is another case of the various types of reaction described earlier. This process results in the formation of a radical site on a polymer chain that may be capable of polymerizing monomers to produce a branched polymer as follows:



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II

THE INITIATING SYSTEMS

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4

Initiation of Vinyl Polymerization by Organic Molecules and Nonmetal Initiators

Ivo Reetz, Yusuf Yagci, and Munmaya K. Mishra

I. INTRODUCTION

Radicals are produced in a special reaction for starting a radical polymerization. Because free radicals are reactive intermediates that possess only very limited lifetimes, radicals are generally produced in the presence of a monomer that is to be polymerized. They react very rapidly with the monomer present. The rate of the reaction of initially formed free radicals with the monomer (the initiation step) is high compared with the rate of radical formation; hence, the latter process is rate determining. Therefore, radical generation by respective initiators is a very characteristic and important feature of radical initiation.

There are mainly three classes of reaction that lead to the generation of free radicals:

- The thermally initiated homolytic rupture of atomic bonds
- The light-induced or radiation-induced rupture of atomic bonds
- The electron transfer from ions or atoms onto an acceptor molecule, which undergoes bond dissociation

Substances that deliver radicals are referred to as initiators. This chapter covers only thermal and redox initiators. Photo and high-energy polymerizations are described in other chapters. Besides polymerizations that

start with the decomposition of the initiator, there are thermally initiated polymerizations in which no initiator is present. In these cases, the monomer (styrene or methyl methacrylate) is itself able to generate initiating sites upon heating. This type of polymerization is also briefly described here.

II. RADICAL GENERATION BY THERMALLY INDUCED HOMOLYSIS OF ATOMIC BONDS

If one works with thermal initiators, the bond dissociation energy is introduced into the polymerization mixture in the form of thermal energy. This energy input is the necessary prerequisite for bond homolysis. Thermolabile initiators are usually employed in a temperature range between 50°C and 140°C. In order to have high initiation rates, the activation energy of thermal initiators has to be on the order of 120–170 kJ mol⁻¹. This activation energy brings about a strong temperature dependence of the dissociation, which is reasonable because initiators should have good storage stability at room temperature but produce radicals at slightly elevated temperatures. There are only a few functional groups meeting these demands. Of practical importance are especially azo compounds and peroxides.

A. Azo Initiators

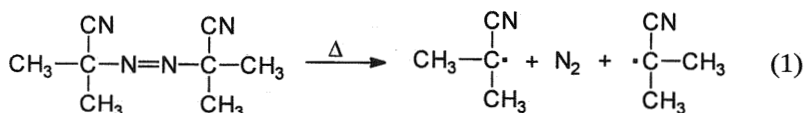
Among azo compounds (RN=NR', R and R' either alkyl or aryl) it is mostly the alkyl and alkyl-aryl derivatives that possess sufficient thermal latency for employing these substances in initiation. Simple azoalkanes decompose at temperatures above 250°C. They are not used as thermal initiators for their relative stability but may be used for photochemical radical production when subjected to ultraviolet (UV) light of appropriate wavelengths ($n-\pi^*$ transition of the N=N double bond). A very great improvement in thermal reactivity is gained by introducing a nitrile group in proximity to the azo link (see Table 1).

The most prominent azo initiator, 2,2'-azo(bisisobutyronitrile), AIBN, is an exceptionally important initiator in industrial polymer synthesis [13,14]. Heated AIBN decomposes giving two 2-cyano-2-propyl radicals and molecular nitrogen. Notably, the generation of the energetically favored and very stable nitrogen molecule must be an important driving force in the decomposition of azo compounds. The activation energy of reaction (1) is only 129 kJ mol⁻¹, whereas the bond dissociation energy of the C—N bond in AIBN is ~300 kJ mol⁻¹. Usually, polymerizations initiated by AIBN are carried out at 50–80°C.

Table 1 Decomposition Characteristics of Selected Azo Compounds

Azo Compound	E_a , kJ mol ⁻¹	k_d , s ⁻¹	Ref.
<chem>CH3-N=N-CH3</chem>	214	-	[1, 2]
<chem>CH3-CH2-N=N-CH2-CH3</chem>	202	-	[3, 4]
<chem>CC(C)(C#N)=N=N(C#N)C(C)C</chem>	142	1.7×10^{-4} (80° C)	[5]
<chem>CCCC(C)(C#N)=N=N(C#N)CCCC</chem>	130	8.7×10^{-5} (80° C)	[5]
<chem>CC1(C)CCCC1C(C#N)=N=N(C#N)C1(C)CCCC1</chem>	-	1.3×10^{-4} (80° C)	[6]
<chem>C1(C)CCCC1C#N=N(C#N)C1(C)CCCC1</chem>	141	7.4×10^{-5} (80° C)	[7]
<chem>C1CCCCC1C(C#N)=N=N(C#N)C1CCCCC1</chem>	148	6.5×10^{-6} (80° C)	[5, 7]
<chem>ClC(C#N)=N=N(C#N)c1ccccc1</chem>	89	5.8×10^2 (12° C)	[8]
<chem>CC(C)(C#N)=N=N(C#N)c1ccccc1</chem>	136	5.4×10^{-5} (100° C)	[9]
<chem>c1ccccc1C(C#N)=N=N(C#N)c2ccccc2</chem>	122	3.5×10^{-4} (55° C)	[10, 11]
<chem>Cc1ccc(cc1)/N=N/C(c2ccccc2)(c3ccccc3)c4ccccc4</chem>	100	2.2×10^{-4} (53° C)	[11]

Note: See also Ref. 12. E_a : activation energy for decomposition; k_d : decomposition rate constant, see Eq. (2).



Heated AIBN decomposes under continuous evolution of initiating radicals following strictly first-order reaction kinetics:



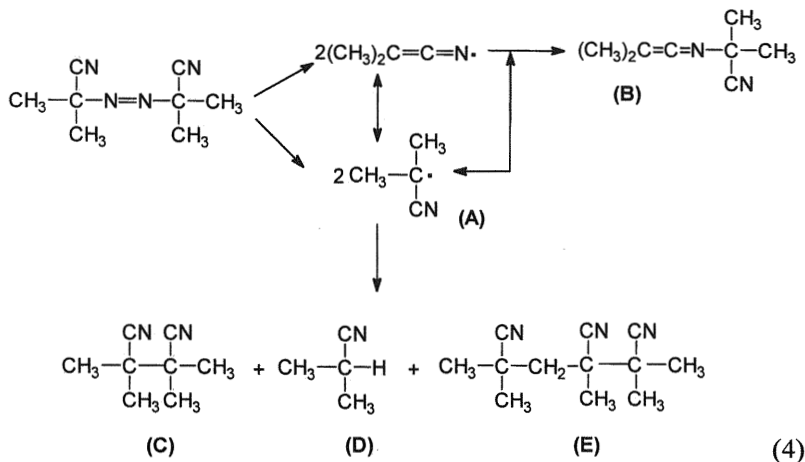
The decomposition rate v_d is expressed as

$$v_d = -\frac{d[\text{I}]}{dt} = k_d[\text{I}] \quad (3)$$

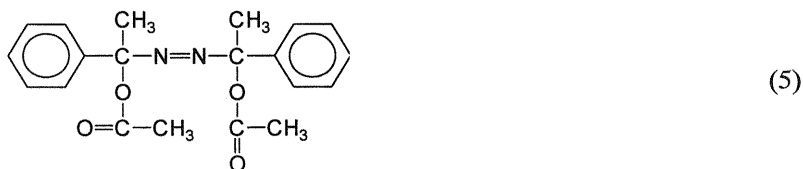
where $[\text{I}]$ is the initiator concentration, t is time, and k_d is the rate constant for the decomposition of the initiator.

For AIBN, k_d does not depend on the solvent. At 50°C , k_d is $\sim 2 \times 10^{-6} \text{ sec}^{-1}$, which in other terms means a half-life of 96 hr.

Not all radicals formed in the decomposition are actually available for reacting with the monomer and initiating the growing of a polymer chain. A considerable loss of radicals is brought about by the so-called cage effect: After the dissociation ($\text{C}-\text{N}$ bond rupture), the radicals formed are still very close to each other, surrounded by solvent molecules (in a solvent cage), which prevents them from diffusing apart. About 10^{-11} sec are necessary for them to move out of the solvent cage. During this short period of time, the radicals collide due to molecular motions and may recombine to give various combination products:



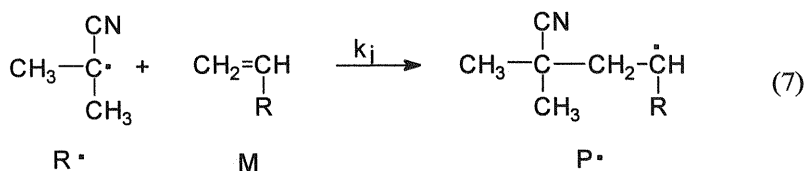
The main product of the cage recombination is a thermally unstable ketimine (**B**), which redecomposes, yielding 2-cyano-2-propyl radicals (**A**). On the other hand, the simultaneously generated tetramethylsuccinonitrile (**C**) is thermally stable and does not yield new radicals upon heating. An investigation of stable combination products of AIBN in toluene has shown that 84% of (**C**), 3.5% of isobutyronitrile (**D**), and 9% of 2,3,5-tricyano-2,3,5-trimethylhexane (**E**) are formed [15]. Hence, about half of the initially formed radicals are consumed this way. Only the remaining portion of radicals, the ones that are able to escape the solvent cage, are actually available for the polymerization. In scientific terms, one speaks of a radical yield U_r (ratio of mole radicals which react with the monomer to mole of initially formed radicals), which is 0.5 for AIBN. The radical yield may be significantly enhanced by introducing bulky substituents. These prevent the recombination of carbon centered radicals in the solvent cage. For example, for 1,1'-diphenyl-1,1'-diacetoxyazoethane, the radical yield amounts to 0.9 (i.e., only 10% of initially formed radicals is consumed by cage reactions):



In general, the rate of radical formation v_r of primary radicals (which are actually available for polymerization) can be written as

$$v_r = 2U_r v_d = 2U_r k_d [I] \quad (6)$$

The initiation step is the addition of primary radicals to the olefinic double bond of the monomer:



By this reaction, the primary radical is incorporated into the growing polymer radical. After the polymerization, it may be detected as a terminal group of the polymer by suitable analytical techniques. The rate of initiation v_i can be expressed as

$$v_i = k_i [R\cdot] [M] \quad (8)$$

If there is a stationary radical concentration and all primary radicals really start a polymerization, the following equations hold:

$$\frac{d[R\cdot]}{dt} = v_r - v_i = 0 \quad (9)$$

$$v_i = 2U_r k_d [I] \quad (10)$$

As Eq. (10) implies, the initiation rate increases with the concentration of the initiator. The faster the initiation, the higher the decomposition rate and, therefore, the radical yield of the initiator. Naturally, it also rises with temperature, because at higher temperature, more radicals are formed. Notably, the molecular weight of the polymer (provided, there is no cross-linking) mostly drops with increasing concentration of primary radicals by whichever means.

As Table 1 shows, among azonitriles, there is a strong influence of the substitution pattern on reactivity. Cyclic azonitriles are somewhat less reactive, an effect which has been attributed to a decreased resonance energy attributable to angular strain in the ring of the 1-cyanocycloalkyl radical. Azotriphenylmethane initiators are extremely thermosensitive, which brings about high radical concentration, but is also connected with relatively poor storage stability. The reactivity of these compounds derives from the resonance stabilization of the triphenylmethyl radical formed. Azotriphenylmethane initiators may also be utilized as photoinitiators, as they possess chromophoric phenyl groups. For emulsion polymerization, water-soluble azo initiators were developed, the hydrophilicity of which was provided by substituents including carboxyl [16], acetate, sulfonates, amide [17], and tertiary amine [18] groups.

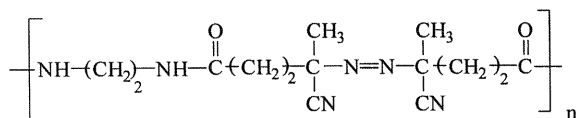
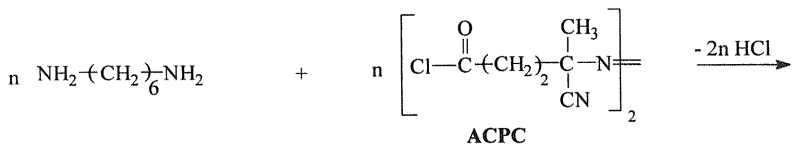
Azo initiators of a special type, namely macro-azo-initiators (MAIs), are of great importance for the synthesis of block and graft copolymers. MAIs are polymers or oligomers which contain azo groups in the main chain, at the end of the main chain, or at a side chain. With the first two initiators, one obtains block copolymers, whereas with the latter, graft copolymers. For the synthesis of MAIs, low-molecular-weight azo compounds are necessary, which have to possess groups that enable monomers to attach to them. Frequently, condensation or addition reactions with the azo compounds listed in Table 2 are used to prepare azo-containing macroinitiators.

For converting these initiators into macroinitiators, diamines, glycols or diisocyanates are often used. Block copolymers of amide and vinyl monomer blocks are easily produced when these macroinitiators are heated

Table 2 Bifunctional Azo Compounds Used Frequently in Polycondensation and Addition Reactions

formula	abbreviation	ref. synthesis	ref. block copolymerization
$\left[\text{HO}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-(\text{CH}_2)_2-\overset{\text{CH}_3}{\underset{\text{CN}}{\underset{ }{\text{C}}}}-\text{N}=\right]_2$	ACPA	[19]	[20-22]
$\left[\text{Cl}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-(\text{CH}_2)_2-\overset{\text{CH}_3}{\underset{\text{CN}}{\underset{ }{\text{C}}}}-\text{N}=\right]_2$	ACPC	[23, 24]	[12, 21, 24-45]
$\left[\text{HO}-(\text{CH}_2)_3-\overset{\text{CH}_3}{\underset{\text{CN}}{\underset{ }{\text{C}}}}-\text{N}=\right]_2$	ACPO	[46]	[47-51]

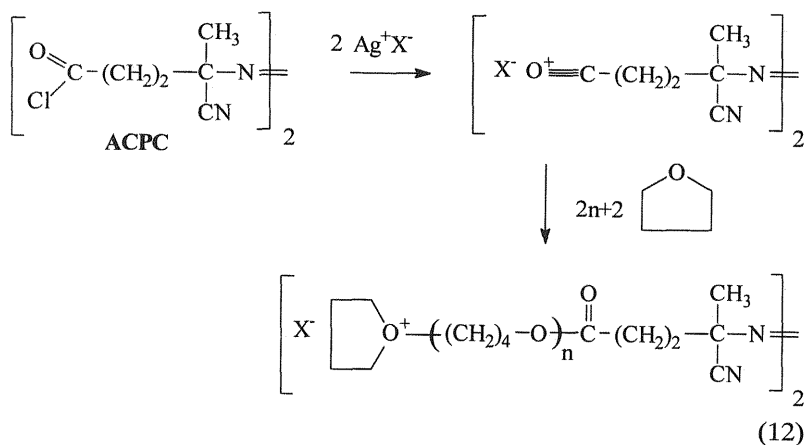
in the presence of a second monomer (this polymerization is a radical vinyl polymerization):



(11)

Besides condensation reactions, the bifunctional ACPC may also be used for cationic polymerization [52–55] (e.g., of tetrahydrofuran). The polymer obtained by the method depicted in reaction (12) contains exactly one central azo bond [56] and is a suitable macroinitiator for the thermally induced block copolymerization of vinyl monomers. Initiators like ACPC are referred to as transformation agents because they are able to initiate

polymerizations of different modes: radical vinyl polymerization (azo site) and cationic or condensation polymerization (chlorocarbonyl group) [55]. Thus, there is a transformation from one type of active center (e.g., cation) to another type (radical) in the course of polymerization, which makes it possible to combine chemically very unlike monomers into one tailor-made block copolymer. There are also several macro-azo initiators that are transformation agents (i.e., possess two different reactive sites) [57]. These may be used for the synthesis of triblock copolymers. There has also been much work on the use of azo initiators in graft copolymerization [58]:

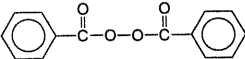
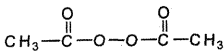
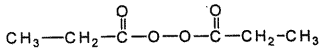
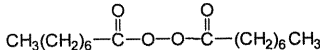
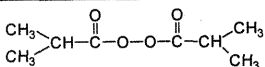
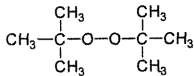
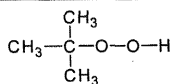
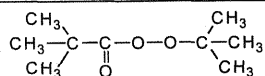
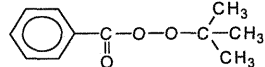
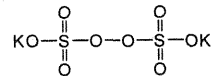


B. Peroxide Initiators

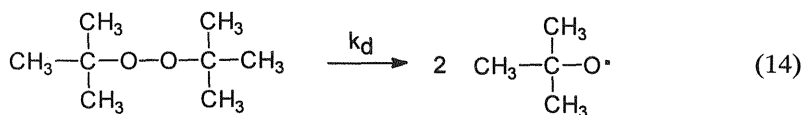
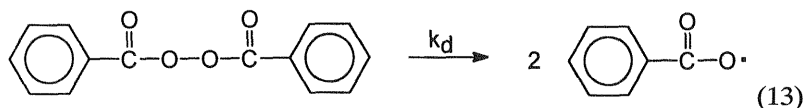
Commercially, peroxides are used as oxidizing, epoxidizing, and bleaching agents, as initiators for radical polymerization, and as curing agents. As far as polymerization and curing are concerned, use is made of the propensity of peroxides for homolytic decomposition. The ease of radical formation is considerably influenced by the substituents at the peroxide group, as is demonstrated in Table 3. For practical applications, diacyl peroxides are used foremost; alkyl hydroperoxides and their esters, peroxyesters, and the salts of peracids are also of importance. As seen in Table 3, in the case of peroxy initiators, there is often a considerable influence of solvent on the decomposition kinetics.

The decomposition of peroxide initiators, which is mostly initiated by heating, involves the rupture of the weak O—O bond, as is illustrated in the example of dibenzoyl peroxide (BPO) and di-*tert*-butyl peroxide.

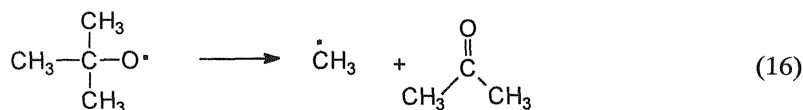
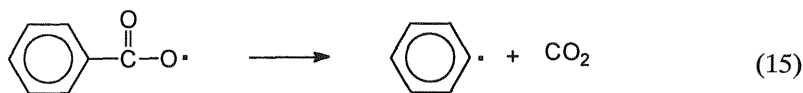
Table 3 Selected Peroxy Compounds as Thermal Free-Radical Initiators

Peroxy Compound	Solvent	E_a , kJ mol^{-1}	k_d , s^{-1}	Ref.
	benzene	124	2.5×10^{-3} (80° C)	[59, 60]
	n-butanol	-	6.1×10^{-4} (80° C)	[61]
	cyclohexane	-	7.7×10^{-5} (80° C)	[61]
	benzene	136	1.6×10^{-4} (85° C)	[62, 63]
	<i>tert</i> -butanol	134	8.7×10^{-5} (80° C)	[64]
	CCl_4	-	4.9×10^{-5} (80° C)	[65]
	benzene	129	2.4×10^{-4} (85° C)	[66]
	benzene	-	3.8×10^{-4} (85° C)	[67]
	benzene	-	2.4×10^{-4} (40° C)	[68]
	benzene	142	7.8×10^{-8} (80° C) $\approx 2.7 \times 10^{-5}$ (130° C)	[69]
	benzene	171	2.0×10^{-5} (170° C)	[70]
	dodecane	128	1.3×10^{-6} (80° C)	[71]
	benzene	120	7.6×10^{-4} (85° C)	[62]
	benzene	145	1.0×10^{-5} (100° C)	[62]
	water		6.9×10^{-5} (80° C)	[72]

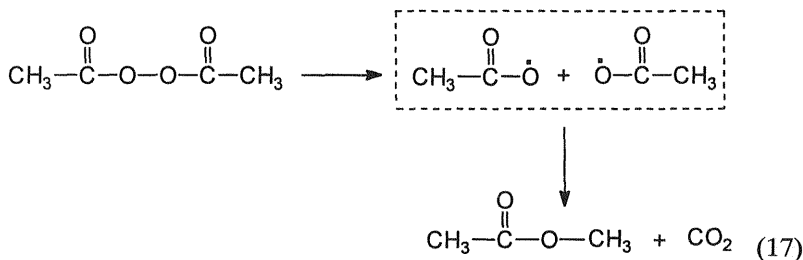
Note: E_a : activation energy for decomposition; k_d : decomposition rate constant, see Eq. (2).



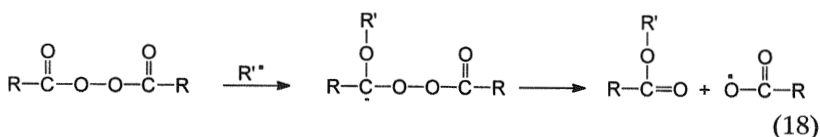
As a rule, the radicals formed in this reaction start the initiation. They are, however, sometimes able to undergo further fragmentation, yielding other radicals:



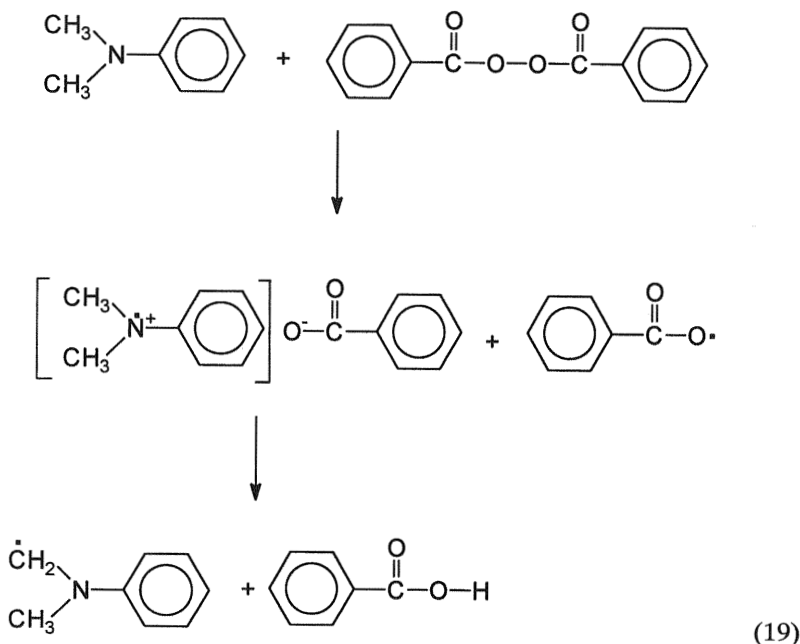
Whether or not a fragmentation according to reactions (15) and (16) takes place depends on the reactivity of the primary formed oxygen-centered radicals toward the monomer. In the case of BPO, there is a fragmentation with phenyl radical formation [reaction (15)] only in the absence of the monomer. In the presence of the monomer, the benzoyl oxy radicals react with monomer before decarboxylation. Aliphatic acyloxy radicals, on the other hand, undergo fragmentation already in the solvent cage whereby recombination products are produced that are not susceptible to further radical formation. As a result, the radical yield U_r for these initiators is smaller than 1:



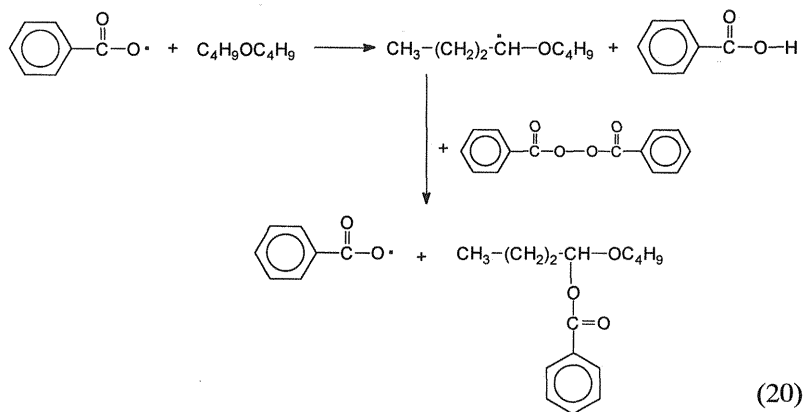
The so-called *induced decomposition* of peroxides is another side reaction leading to a diminished radical yield. In the case of acylperoxides, primary formed radicals may attack the carbonylic oxygen atom of diacyl peroxides, leading to the formation of a carbon-centered radical:



The decomposition of dibenzoyl peroxide in dimethylaniline is extremely fast, which is also due to induced decomposition. The reaction mechanism involves the formation of radical cation and a subsequent transformation into radicals and stable species. In polymer synthesis, small quantities of dimethylaniline are sometimes added to BPO to promote radical generation:



Another example is the induced decomposition in the presence of butyl ether. In this case, the reaction is very likely to involve the formation of α -butoxy butyl radicals:



Usually, in the case of induced decomposition, one initiating molecule disappears without the formation of two radicals. What would be possible if the initiator species would undergo dissociation? In other words, the total number of radicals is smaller for the induced decomposition, not higher as sometimes assumed. The consumption of the initiator is, at the same time, faster than the normal dissociation. In fact, the decomposition of the initiator is faster than one would follow from first-order reaction kinetics:

$$-\frac{d[\text{I}]}{dt} = k_d[\text{I}] + k_{\text{ind}}[\text{I}]^x \quad (21)$$

As reactions (18–20) imply, the mechanism of induced decomposition does very much depend on the solvent. Furthermore, the extent to which it occurs changes with the type of peroxy initiator used and the monomer itself, because often induced decomposition may be triggered by any of the radicals present in the reaction mixture.

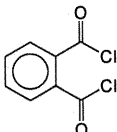
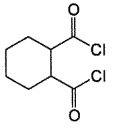
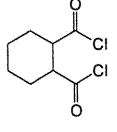
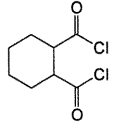
The choice of the proper peroxy initiator largely depends on its decomposition rate at the reaction temperature of the polymerization. BPO is the major initiator for bulk polymerization of polystyrene or acrylic ester polymers, where temperatures from 90°C to 220°C are encountered. Dilauroyl, dicaprylyl, diacetyl, and di-*tert*-butyl peroxides are also used. In the case of suspension polymerization of styrene, where temperatures between 85°C and 120°C are applied, the initiators also range in activity from BPO to di-*tert*-butyl peroxide. In suspension polymerization of vinyl chloride (reaction temperatures of 45–60°C for the homopolymer), thermally very labile peroxides such as diisopropyl peroxydicarbonate and *tert*-butyl peroxy-pavilate are used.

As far as the handling of peroxides is concerned, it must be noted that upon heating, peroxides may explode. Special precautions have to be taken

with peroxides of a low carbon content, such as diacetyl peroxide, as they are often highly explosive. In the pure state, peroxides should be handled only in very small amounts and with extreme care. Solutions of high peroxide content are also rather hazardous.

Besides low-molecular-weight peroxides, there are also numerous works on macromolecular peroxide initiators, which are useful in the preparation of block copolymers [73]. As illustrated in Table 4, various compounds have been reacted via condensation or addition reaction to yield macro-peroxy-initiators.

Table 4 Macroinitiators Having Peroxy Groups Synthesized from Two Components

Structure of Peroxide Group	Reactant A	Reactant B	Ref.
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{O}-\text{C}- \end{array}$	H-O-O-H		[74]
		$\text{Cl}-\text{C}(=\text{O})-(\text{CH}_2)_n-\text{C}(=\text{O})-\text{Cl}$	[75]
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{O}- \end{array}$	$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ \quad \quad \\ \text{H}-\text{O}-\text{O}-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{O}-\text{O}-\text{H} \\ \quad \quad \\ \text{CH}_3 \quad \quad \text{CH}_3 \end{array}$		[76]
		$\text{Cl}-\text{C}(=\text{O})-(\text{CH}_2)_n-\text{C}(=\text{O})-\text{Cl}$	[77]
	$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ \quad \quad \\ \text{H}-\text{O}-\text{O}-\text{C}-\text{C}=\text{C}-\text{C}-\text{O}-\text{O}-\text{H} \\ \quad \quad \\ \text{CH}_3 \quad \quad \text{CH}_3 \end{array}$		[76]
	$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ \quad \quad \\ \text{H}-\text{O}-\text{O}-\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{O}-\text{O}-\text{H} \\ \quad \quad \\ \text{CH}_3 \quad \quad \text{CH}_3 \end{array}$		[76]

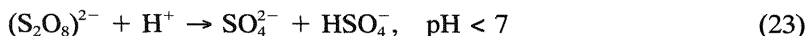
Note: See also Ref. 73.

As far as the decomposition of macro-peroxy-initiators is concerned, it has been found that the decomposition rate is about the same as for structurally similar low-molecular-weight peroxy initiators [73], despite the cage effect that obviously leads to some propensity to recombination reactions. High-molecular-weight peroxy initiators have been mostly used to combine two monomers which polymerize by radical addition polymerization. Examples are block copolymers consisting of a polyacrylamide block and a random polyacrylamide copolymer as a second block [78–82], and block copolymers of polymethyl methacrylate/poly vinyl acetate [83,84], polystyrene/polyacrylonitrile [85], and polystyrene/polyhydroxymethyl acrylate [86]. In block copolymerization, the good solubility, especially of aliphatic macroperoxyinitiators in common monomers, is being used. Block copolymers prepared by macro-peroxy-initiators often show interesting surface activity (useful for coatings and adhesives). Further, they find application as antishrinking agents [87–89] and as compatibilizers in polymer blends.

C. Persulfate Initiators

Persulfate initiators generate free radicals upon the thermally induced scission of O—O bonds, thus resembling the organic peroxides dealt with above. For potassium persulfate, the decomposition rate constant is $9.6 \times 10^{-5} \text{ sec}^{-1}$ at 80°C and the activation energy amounts to 140 kJ mol^{-1} (in $0.1 \text{ mol L}^{-1} \text{ NaOH}$) [90].

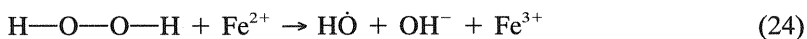
Interestingly, there are quite different reactions depending on the pH of the reaction media. In alkaline and neutral media, two radical anions are formed from one persulfate molecule. In strongly acidic surrounding, however, no radicals are generated, giving rise to a suppression of polymerization with lowering the pH:



The fact that the peroxydisulfate ion may initiate polymerization of certain vinyl monomers has been known for some time [91]. In most practical polymerizations however, peroxysulfate is used together with reducing agent in redox-initiating systems.

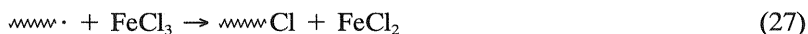
III. RADICAL FORMATION VIA ELECTRON TRANSFER—REDOX-INITIATING SYSTEMS

Oxidation agents, such as hydroperoxides or halides, in conjunction with electron donors, like metal ions, may form radicals via electron transfer:

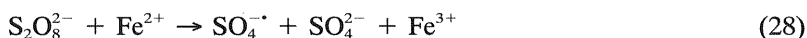


The initiator systems used in this type of polymerization consists, therefore, of two components: an oxidizing agent and a reducing agent. If hydrogen peroxides are used as the oxidizing agent, one hydroxyl radical and one hydroxyl ion are formed, in contrast to direct thermal initiation, where two hydroxyl radicals are generated (*vide ante*). The hydroxyl ion formed in redox systems is stabilized by solvation. As a result, the thermal activation energy is relatively low, usually 60–80 kJ mol⁻¹ lower than for the direct thermal activation. Therefore, using redox systems, polymerizations can be conducted at low temperatures, which is advantageous in terms of energy saving and prevention of thermally induced termination or depolymerization. In technical synthesis, peroxide-based redox systems are used, for example, for the copolymerization of styrene and butadiene at 5°C, the so-called cold rubber process, and for the polymerization of acrylonitrile in the aqueous phase. In addition to peroxides, there are many other oxidizing agents that may be used in radical polymerization. Table 5 gives an idea of the variety of systems being used.

If metal ions are used as the reducing agent, there is a danger of contaminating the polymer with heavy metals, which may be a source of easy oxidizability of the polymer. Furthermore, high concentrations of metal ions in their higher oxidation state may lead to termination reactions according to



In order to keep the concentration of metal salt small, additional reducing agents are added, which react with the metal ion, as demonstrated in the example of the system potassium peroxidesulfate, sodium sulfite and ferrous sulfate in reactions (28) and (29):



Because the rate of reaction (29) is very high compared with that of reaction (28), Fe³⁺ ions formed are instantaneously reduced to Fe²⁺, which allows the use of only catalytic quantities of iron salt for initiation. The redox system depicted in reactions (28) and (29) is used in the above-mentioned technical polymerization of acrylonitrile. In the cold rubber process, systems consisting of hydroperoxide, ferrous salts, and rongalite are used.

Table 5 Initiating Systems in Redox Initiation

Oxidizing Agent	Initiating Radical	Reducing Agent	Ref.
H—O—O—H	HO	Fe ²⁺	[92-94]
		NO ₃ ⁻	[95]
		NO ₂ ⁻	[95]
		NH ₃	[94]
		HSO ₃ ⁻ /SO ₃ ²⁻	[91]
		$\text{HS}-\text{C}(\text{NH}_2)=\text{NH}$	[96-98], see also [28]
R—O—O—R	RO [•]	Fe ²⁺	[99-101]
		$\text{HS}-\text{C}(\text{NR})=\text{NHR}$	[98, 102-103]
	$\text{RO}^{\bullet} + \text{CH}_2=\text{N}(\text{CH}_3)-\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5-\text{N}(\text{CH}_3)_2$	[104] see also [15]
R—O—O—H	RO [•]	Fe ²⁺	[105, 106]
	R [•]	BR ₃	[107] see also [26], [27]
O ₂	R [•]	BR ₃	[107] see also [26], [27]
Br ₂	Br [•]	Fe ²⁺	[108]
	Br [•] and $\cdot\text{S}-\text{C}(\text{NH}_2)=\text{NH}$	$\text{HS}-\text{C}(\text{NR})=\text{NHR}$	[109]
S ₂ O ₈ ²⁻	SO ₄ ^{-•}	Ag ⁺	[95, 110]
		Fe ²⁺	[111]
		$\text{HS}-\text{C}(\text{NH}_2)=\text{NH}$	[98]
H ₂ P ₂ O ₈ ²⁻	HPO ₄ ^{-•}	Ag ⁺	[112]
		S ₂ O ₃ ²⁻	[113]
$\text{C}_6\text{H}_5-\text{N}(\text{CH}_3)_2$	Cu ²⁺	$\text{C}_6\text{H}_5-\text{N}(\text{CH}_3)\text{CH}_2^{\bullet}$	[114]

For initiating radical polymerization at temperatures as low as -50°C to -100°C , boroalkyles are applied as reducing agents [107]. Upon reaction with oxygen or with organic hydroperoxides, they are able to abstract alkyl radicals which act as initiating species. The alkyl radicals generated are of extraordinary reactivity, as they are usually not stabilized by resonance. Therefore, a number of side reactions, such as chain transfer, may occur:



Thiourea derivatives are another often used reducing agent, which is able to produce radicals upon reaction with peroxides and other oxidizing agents. Upon this reaction, both sulfur-centered radicals and radicals stemming from the oxidizing agent are formed. In the polymerization of methylmethacrylate with the hydrogen peroxide/thiourea system, both amino and hydroxyl end groups were found, of which the latter predominate [98]. If bromine was used as the oxidizing agent, end-group analysis implied that the sulfur-centered radical is the major initiating species [109]:



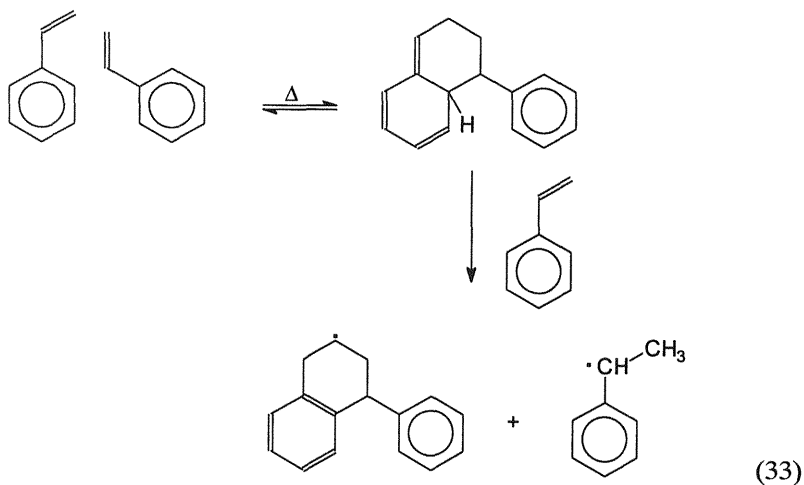
With many redox systems, coupled reactions take place that make it necessary to choose the appropriate system in accordance with the monomer and the polymerization conditions. If the redox reaction is slow, there will be a low yield of radicals and therefore a low polymerization rate. On the other hand, if the redox reaction is fast compared with the initiation step, the majority of initiating radicals will be consumed by radical termination reactions. Therefore, redox systems are modified by further additives. For example, heavy metal ions may be complexed with substances such as citrates, which adjust their reactivity to a reduced level. Hence, redox systems for technical polymerization are complex formulations which enable one to obtain optimum results at well-defined reaction conditions.

IV. THERMALLY INDUCED RADICAL FORMATION WITHOUT INITIATOR

In general, an initiator is added to vinyl monomers in order to produce initiating radicals upon the desired external stimulation. Indeed, most impurity-free vinyl polymers do not initiate upon heating, making it unavoi-

able to introduce free-radical initiators. However, monomers like styrene and methyl methacrylate derivatives may polymerize without any added initiator. The mechanism involves the spontaneous formation of radicals in the purified monomers.

For styrene, the conversion of monomer per hour rises from $\sim 0.1\%$ at 60°C to about 14% at 140°C . Thus, the effect has to be encountered, especially for polymerizations at higher temperatures. Furthermore, when a styrene-based monomer is to be purified by distillation, the addition of inhibitors and distillation at reduced pressure is advisable in order to avoid the distillate from becoming viscous. Another difficulty occurring during distillation is the formation of polymer in the column, which can also be prevented by distilling in vacuo. The initiation of a styrene-based monomer is assumed to involve a (4+2) cycloaddition of the Diels–Alder type with a subsequent hydrogen transfer from the dimer to another monomer molecule:



The radicals thus generated initiate the polymerization, provided they do not deactivate by mutual combination or disproportionation. Due to their low ceiling temperature, α -substituted styrenes hardly undergo thermal polymerization in the absence of initiator.

With methyl methacrylate, thermal self-polymerization also occurs, but with a rate about two orders of magnitude smaller than with styrene.

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5

Chemical Initiation by Metals or Metal-Containing Compounds

Yusuf Yagci, Ivo Reetz, and Munmaya K. Mishra

I. INTRODUCTION

The initiation by metals and metal-containing compounds generally takes place as a redox process [1]. In this type of initiation, free radicals responsible for polymerization are generated as transient intermediates in the course of a redox reaction. Essentially, this involves an electron transfer process followed by scission to give normally one free radical. The oxidant is generally referred to as the initiator or the catalyst, and the reducing agent is called the activator or the accelerator. Notably, depending on its oxidation state, the metal can act as reducing or oxidizing agent.

The special features of redox initiation are as follows:

- (a) Very short (almost negligible) induction period.
- (b) A relatively low energy of activation (in the range of 10–20 kcal mol⁻¹) as compared with 30 kcal mol⁻¹ for thermal initiation. This enables the polymerization to be carried out at a relatively low temperature, thereby decreasing the possibility of side reactions, which may change the reaction kinetics and the properties of the resulting polymer.
- (c) The polymerization reaction is controlled with ease at low temperature, and comparatively high-molecular-weight polymers with high yields can be obtained in a very short time.

- (d) There is convenient access to a variety of tailor-made block copolymers.
- (e) Redox polymerizations also provide direct experimental evidence for the existence of transient radical intermediates generated in redox reactions, which enables the identification of these radicals as terminating groups, helping to understand the mechanism of redox reactions.

A wide variety of redox reactions between metals or metal compounds and organic matter may be employed in this context. Because most of them are ionic in nature, they may be conveniently carried out in aqueous solution and occur rather rapidly even at relatively low temperatures. As a consequence, redox systems with many different compositions have been developed into initiators that are very efficient and useful, particularly for suspension and emulsion polymerization in aqueous media [2], which is dealt with in detail in Chapter 6. The low-temperature (at $\sim 5^\circ\text{C}$) copolymerization of styrene and butadiene for the production of GR-S rubber was made possible with the success of these catalytic systems.

Commonly used oxidants in redox polymerization include peroxides, cerium(IV) salts, sodium hypochloride, persulfates, peroxydiphosphate, and permanganate. Reducing agents are, for example, the salts of metals like Fe^{2+} , Cr^{2+} , V^{2+} , Ce^{2+} , Ti^{3+} , Co^{2+} , Cu^{2+} , oxoacids of sulfur, hydroxyacids, and so forth.

A typical example of a redox initiation with a metal compound as activator is the initiation by the system H_2O_2 and ferrous(II) salts [3]. In the course of this reaction, hydroxy radicals are evolved which are very reactive initiators. The reaction scheme is as follows:



In the subsequent sections, redox reactions involving metal carbonyls, metal chelates and ions, and permanganate as reducing agents will be reviewed. The other redox systems applied for suspension polymerization are the subject of Chapter 6.

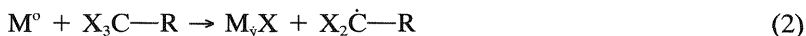
II. TYPES OF INITIATION

A. Initiation by Metal Carbonyls

1. Thermal Initiation

It is well known from extensive electron-spin resonance (ESR) studies [4–6] that organic halides in conjunction with an organometallic derivative of a transition element of groups VIA, VIIA, and VIII, with the metal in a low

oxidation state, give rise to free-radical species. Kinetic studies of the initiation of polymerization [7,8] have revealed that in all systems containing organometallic derivatives and organic halides, the radical-producing reaction is basically an electron transfer process from transition metal to halide as presented in the following equation (M being the transition metal):



In this process, the organic halide is split into an ion and a radical fragment. Free-radical formation by oxidation of molybdenum carbonyl with carbon tetrachloride and carbon tetrabromide has been studied in detail [6]. The overall reaction may be represented as follows:

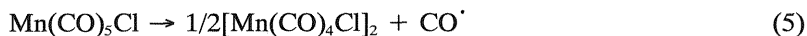


Manganese pentacarbonyl chloride has also been used [9] as a thermal initiator for free-radical polymerization in the presence of halide and non-halide additives. At 60°C, it is 10 times as active as azobisisobutyronitrile toward methyl methacrylate polymerization. In the absence of additives, manganese pentacarbonyl chloride does not initiate the polymerization of methyl methacrylate significantly at temperatures up to 80°C; even at 100°C, initiation is very slow. Analysis of the polymers produced shows that, with CCl_4 as the additive, initiation occurs through CCl_3 radicals and no manganese is found in the polymers. Angelici and Basolo [10] have reported measurements of the rates of ligand exchange reactions undergone by $Mn(CO)_5Cl$ and have concluded that the rate-determining step is dissociation:

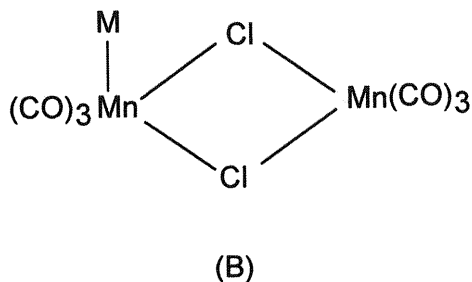
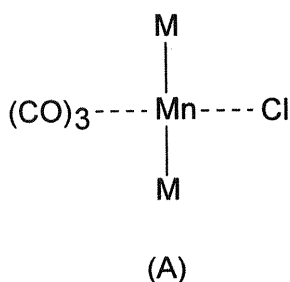


The preceding reaction is followed by the rapid combination of $Mn(CO)_4Cl$ with the ligand L so that the overall process is the replacement of CO by L.

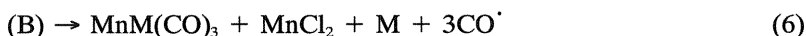
Bamford et al. [11] have shown that $Mn(CO)_5Cl$ is a very reactive solution, even in nonpolar solvents. Thus, in benzene solution at 25°C, the dimer $(Mn(CO)_4Cl)_2$ is readily formed if carbon monoxide is removed by evacuation or a stream of nitrogen:



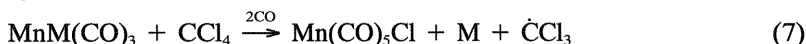
In a donor solvent such as methyl methacrylate, ligand exchange occurs at 25°C and monomeric and dimeric complexes such as (A) and (B) are produced [11]:



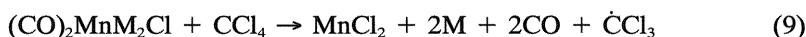
The radicals may be generated from thermal decomposition of (B) according to the



In the presence of CCl_4 , the reaction may be presented as follows:

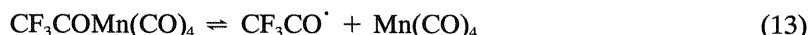
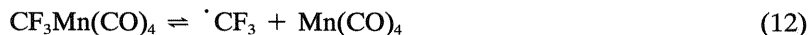


An alternative initiation mechanism starting from the intermediate (A) also involves radical generation on the halide.



Bamford and Mullik [12] had reported the methyl methacrylate radical polymerization initiated by the thermal reactions of methyl and acetyl manganese carbonyls. The initiating species are claimed to be methyl radicals formed from the reaction of methyl methacrylate with the transition metal derivative through an activated complex. In the presence of additives such as CCl_4 and C_2F_4 , however, initiating radicals are derived from the additives as was proved by the analysis of the resulting polymers (i.e., initiation by CCl_3 radicals would introduce three chlorine atoms into each polymer chain).

In the case of perfluoromethyl and perfluoroacetyl manganese carbonyls [13], the initiating mechanism does not involve complexation with the monomer, as illustrated in Eqs. (10)–(13) for perfluoromethyl manganese carbonyl:



Tetrakis(triphenyl phosphite)nickel (NiP_4) is an interesting example of

the large class of organometallic derivatives which, in the presence of organic halides, initiate free-radical polymerization [5]. It was shown that the kinetics of initiation at room temperature are consistent with a mechanism in which ligand displacement by monomer leads to a reactive species readily oxidized by the halide [14–16].

The generation mechanism of the initiating radicals species is reported in Eqs. (14)–(16):

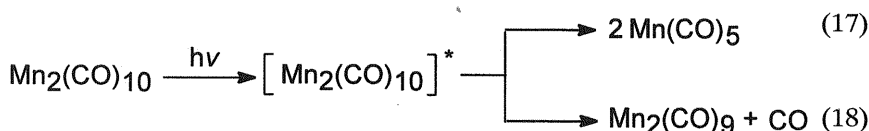


in which M represents the monomer and n is the number of radicals arising from reaction of a single molecule of complex. Notably, each complex yields approximately one free radical. Detailed studies [17] on the preceding system using methyl methacrylate and styrene as monomer revealed that both monomers behave similar in dissociation and complexation steps. But the reaction between the $\text{M} \cdots \text{NiP}_3$ complex and carbon tetrachloride shows marked kinetic differences in the two systems.

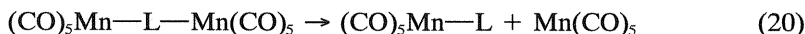
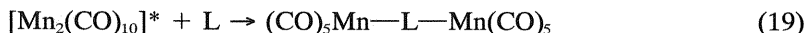
2. Photochemical Initiation

Two different types of photochemical initiation based on transition metal carbonyls in conjunction with a coinitiator were proposed [18]. Both systems require a “coinitiator.” In the case of Type 1 initiation, the coinitiator is an organic halide while Type 2 initiation is effective with a suitable olefin or acetylene.

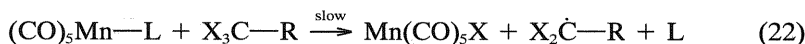
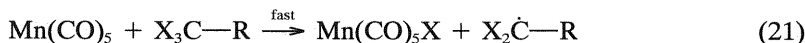
Type 1 Initiation. The basic reaction (2), described for the metal carbonyl-initiating system, may occur thermally and photochemically. Among all the transition metal derivatives studied, manganese and rhenium carbonyls $[\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$, respectively], which absorb light at rather long wavelengths, are the most inconvenient derivatives for the photoinitiation. The initiating systems $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ and $\text{Re}_2(\text{CO})_{10}/\text{CCl}_4$ were first studied by Bamford et al. [19,20]. These authors reported that quantum yields of initiation under appropriate conditions were close to unity. As in the thermal initiation [see reaction (2)], the principal radical-generating reaction is an electron transfer from transition metal to halide, the former assuming a low oxidation state (presumably the zero state). Whether electronically excited metal carbonyl compounds can react directly with halogen compounds has not been determined. From flash photolysis studies, it was inferred that electronically excited $\text{Mn}_2(\text{CO})_{10}$ decomposes in cyclohexane or n -heptane via two routes, both being equally important:



According to Bamford [21,22], excited manganese carbonyl can react with a "coordinating compound" L in the following way:

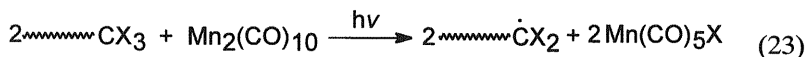


Both products of reaction (20) are capable of undergoing dissociative electron transfer with appropriate organic halides. The rate constants, however, are different:



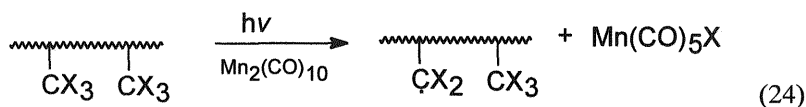
A similar mechanism [23] could hold for $\text{Re}_2(\text{CO})_{10}$; in this case, the vinyl monomer used in the system may function as the coordinating compound L. In all these systems studied, the rate of radical generation strongly depends on the halide concentration. Apparently, there is no initiation when no halide is present. With increasing halide concentration, the rate increases and reaches a plateau value such that the rate is not affected by halide concentration. For practical applications, it was advised to use minimum halide concentration at the plateau condition. The reactivity of halides increases with multiple substitution in the order $\text{CH}_3\text{Cl} < \text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$ and with introduction of electron-withdrawing groups. Bromine compounds are much more reactive than the corresponding chlorine compounds and saturated F and I compounds are ineffective.

The metal carbonyl photoinitiating system has been successfully applied to the block copolymer synthesis [18]. In this case, prepolymers having terminal halide groups are irradiated in the presence of $\text{Mn}_2(\text{CO})_{10}$ to generate initiating polymeric radicals:



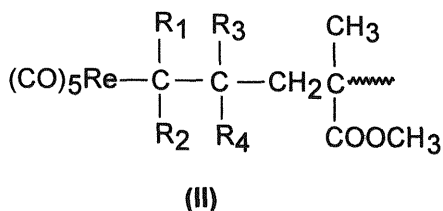
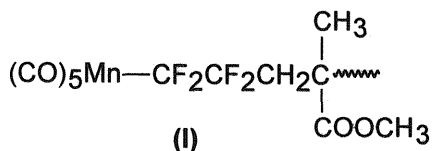
Notably, low-molar-mass radicals are not formed and homopolymerization cannot occur. Moreover, metal atoms do not become bound to the polymer in these processes. Polymeric initiators with terminal halide groups can be prepared in different ways. Anionic polymerization [24,25], group transfer polymerization [26], metal carbonyl initiation [27], chain transfer reaction

[28], condensation reactions [29], and functional initiator [30] approaches have been successfully applied for halide functionalization and a wide range of block copolymers were prepared from the obtained polymers by using metal carbonyl photoinitiation. A similar approach [18] to obtain graft copolymers involves the use of polymers possessing side chains with photoactive halide groups:



The grafting reaction leads to the synthesis of a network if combination of macroradicals is the predominant termination route. Network formation versus grafting of branches onto trunk polymers has been intensively studied using poly(vinyl trichloroacetate) as the trunk polymer. Styrene, methyl methacrylate, and chloroprene were grafted onto various polymers, including biopolymers [31–34]. These examples illustrate the broad versatility of the method. Actually, any blocking and grafting reactions by using this method appear feasible, provided suitable halide-containing polymers are available. In this connection, the reader's attention is also directed to previous reviews devoted to photoblocking and photografting [18,35].

Type 2 Initiation. Bamford and Mullik [36] reported that pure tetrafluoroethylene is polymerized at -93°C upon irradiation in the presence of a low concentration of $\text{Mn}_2(\text{CO})_{10}$ or $\text{Re}_2(\text{CO})_{10}$. On the basis of this observation, other common vinyl monomers such as styrene and methyl methacrylate were photopolymerized at ambient temperatures with the systems $\text{Mn}_2(\text{CO})_{10}/\text{C}_2\text{F}_4$ and $\text{Re}_2(\text{CO})_{10}/\text{C}_2\text{F}_4$. This method was also used for cross-linking and surface grafting [37,38]. The polymers obtained this way possess metal atoms, as illustrated below for polymethylmethacrylate.



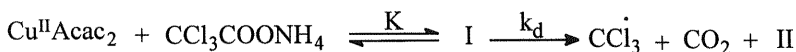
B. Initiation by Metal Complexes

Chelate complexes of certain transition metal ions can initiate free-radical polymerization of vinyl monomers.

Some of the important systems such as Cu II–acetylacetonate in dimethylsulfoxide for polymerization of methyl methacrylate [39], Cu II–chitosan for methyl methacrylate and acrylonitrile polymerization [40], Cu II–(vinylamino–vinylacetamide) copolymer [41], Cu II–(α,ω -diaminoalkane) [42], and Cu II–imidazole [43] for acrylonitrile polymerization, and Cu II–amine in CCl_4 for acrylonitrile and methyl methacrylate polymerization [44], Mn III–acetylacetonate for vinyl chloride polymerization [45], Mn III, Co III, and Fe III–acetylacetonate for methyl methacrylate polymerization [46], Ni II–bis(acetylacetonate)–($\text{Et}_3\text{Al}_2\text{Cl}_3$) for isoprene polymerization [47], vanadyl acetylacetonate–tributyl borane for methyl methacrylate polymerization [48], Cu II–polyvinylamine for acrylonitrile and methyl methacrylate polymerization [49,50], and Cu II–acetylacetonate with ammonium trichloroacetate [51], Cu II–bis-ephedrine [52] in CCl_4 , and Mn III–acetylacetonate [53] for the polymerization of various vinyl monomers have already been reported.

Some of the copolymerization reactions using metal complexes were also a subject of interest for various groups of workers [54–56]. All the investigators predicted the initiation process to be essentially the scission of a ligand as free radical, with the reduction of the metal to a lower valency state. The reduction of the metal ion was confirmed by spectral and ESR measurements. It has also been illustrated that the ability of the metal chelates for the polymerization of vinyl monomers could be enhanced by the addition of various foreign substrates, particularly halogen-containing compounds [57–60] and compounds of electron-donating [61–63] or electron-accepting [53] properties. In the majority of cases reported so far, polymerization proceeded through typical radical processes.

Allen [64] reported vinyl polymerization using ammonium trichloroacetate and bis-acetylacetonate–Cu II. On the basis of the result at 80°C proposed by Bamford et al. [51] that when ammonium trichloroacetate was not in excess, the actual initiation was a 1:1 complex of two components decomposing to give the trichloromethyl radical by an internal electron-exchange reaction:

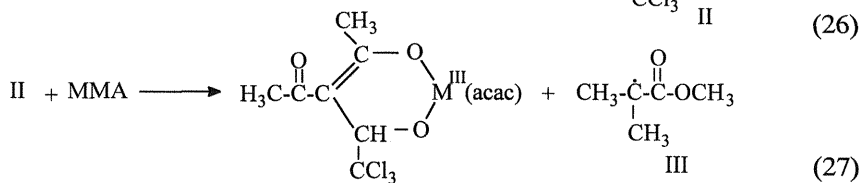
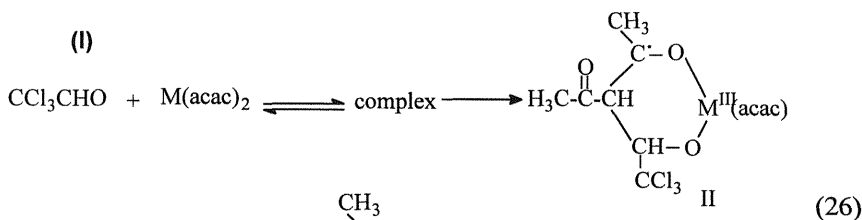


where II is an unspecified CuI complex. A possible structure for formula (I) was suggested:



The trichloromethyl radical was the only initiating radical proved by other workers [52,65].

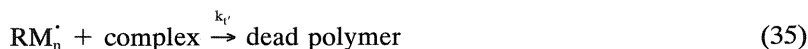
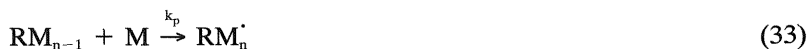
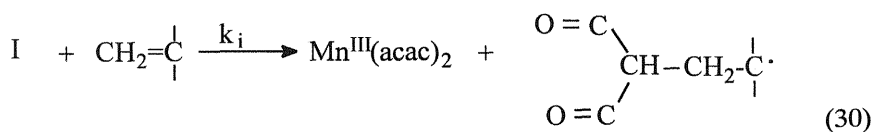
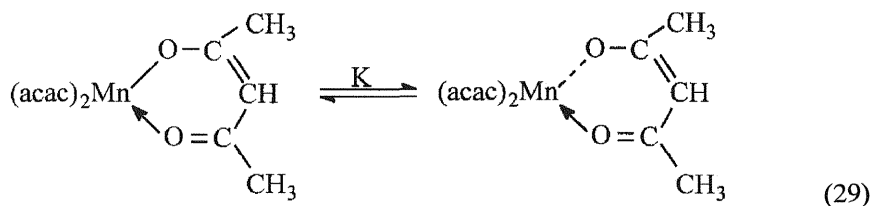
Uehara et al. [66] also reported the polymerization of methyl methacrylate initiated by bis(acetylacetonato) metal(II) and chloral, where the metal M is either Mn(II) or Co(II). It can be frequently seen that the activity of a metal complex as an initiator of radical polymerization increases in the coexistence of an organic halide. This effect was attributed to the redox reaction between the metal complex and the organic halide [67–69]. The mechanism may be presented as



The addition of chloral to the Co(II) complex indicates the transformation from octahedral to tetrahedral symmetry [70], supporting the formation of complex I.

In the polymerization of acrylonitrile of $\text{Mn}(\text{acac})_3$, the initiation mechanism is considered to occur through the homolytic fission of the metal-oxygen bonds, as pointed out by Arnett and Mendelsohn [71]. This mechanism is also supported by Bamford and Lind [72].

The first step is the formation of activated species (I) in equilibrium with $\text{Mn}(\text{acac})_3$. On reaction with the monomer, it yields the radical that initiates the polymerization. The reaction scheme is as:

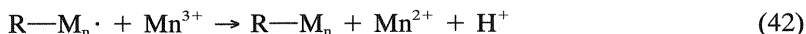
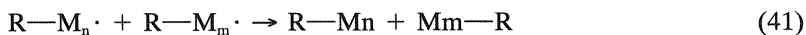


C. Initiation by Metal Ions

1. Manganese (III)

The oxidation of various organic substrates using Mn^{3+} for the initiation of free-radical polymerization has been extensively studied [73–90]. In almost all the systems studied, initiating radicals are postulated to be formed from the decomposition of the complex between Mn^{3+} and organic substrate as depicted in Eqs. (36)–(42). This mechanism also considers the mutual termination of growing radicals.





In the polymerization of acrylonitrile [77] in which organic acids were employed as the reducing agent, the order of reactivity of the acids has been found to be

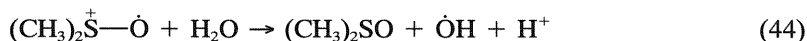
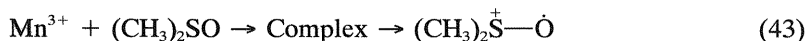
citric > tartaric > ascorbic > oxalic > succinic > glutaric > adipic

Similar studies concerning the comparison of alcohol reactivity for the polymerization of methyl methacrylate were also performed by Nayak and co-workers [83]. The order of the reactivity of alcohols for the Mn^{3+} –alcohol redox couple was found to be in the following order:

1-propanol > glycerol > ethylene glycol > isobutyl alcohol
 > 1-butanol > 1,2-propanediol > cycloheptanol > cyclohexanol
 > cyclopentanol

Polymerization of methyl methacrylate with the $\text{Mn}(\text{OH})_3$ –hydrazine system was investigated by two independent groups. Bond et al. [84] found that the rate of polymerization at constant $\text{Mn}(\text{OH})_3$ concentration was independent of the monomer concentration and varied with the pH and temperature. Rehmann and Brown [85,86] applied the same system to the emulsion polymerization of methyl methacrylate and reported that the rate of polymerization was proportional to surface area of $\text{Mn}(\text{OH})_3$ formed in the system.

The redox polymerization of acrylonitrile initiated by dimethylsulfoxide– Mn^{3+} in H_2SO_4 and HClO_4 was investigated by Devi and Mahadevan [87–89]. Trivalent manganese forms a complex with dimethyl sulfoxide, followed by a reversible electron transfer. The radicals formed from the dissociation radical ion initiates the polymerization:



The rate of polymerization varied directly with the dimethylsulfoxide concentration and was proportional to the square of the monomer and independent of the oxidant. They also investigated the polymerization of methyl methacrylate with Mn^{3+} and reducing agents such as dimethyl sulfoxide, diacetone alcohol, and malonic acid. All the reducing agents formed the complexes of varying stability with Mn^{3+} , from which initiating species are produced.

The efficiency of the cyclohexanone/ Mn^{3+} redox system for the polymerization of acrylonitrile and methyl methacrylate in perchloric acid and sulfuric acid media was investigated [81]. It was found that the rate of polymerization was independent of the oxidant concentration and varied linearly with the monomer and reducing agent concentration. Complex formation and termination mechanism was found to be different in two acidic media. In perchloric media, the termination is effected by the oxidant, whereas in sulfuric acid, primary radicals terminate growing chains.

Drummond and Waters [90] employed various organic substrates as reducing agent in Mn^{3+} pyrophosphate-based redox system.

An interesting variation of the Mn^{3+} /organic substrate redox method applies to grafting methyl methacrylate onto cellulose and polyvinylalcohol [91,92]. The method has also been applied to graft vinyl monomers onto collagen [93]. Cakmak [94] described the use of manganese acetate redox system for block copolymerization of acrylonitrile with polyacrylamide. In this case, terminal carboxylic groups incorporated to polyacrylamide acted as the reducing agent.

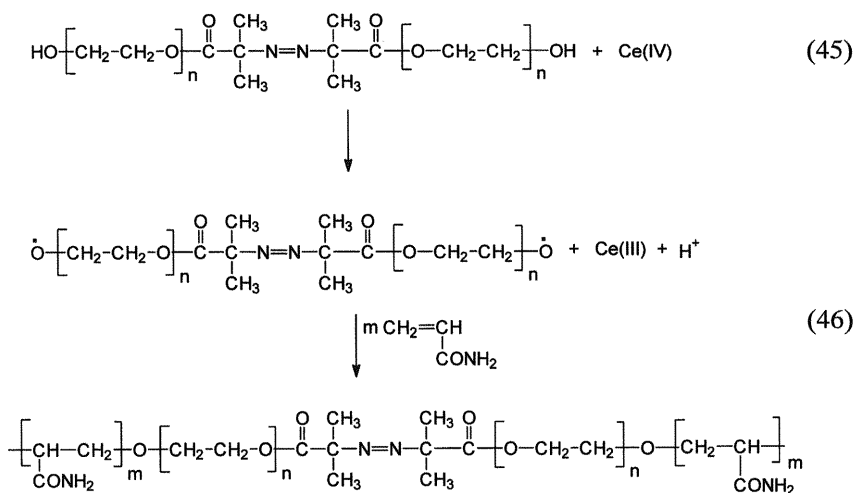
2. Cerium(IV)

For initiating vinyl polymerizations, Ce^{4+} ions alone [95–105] or in conjunction with suitable reducing agents which include formaldehyde [106,107], malonic acid [108], dextran [109], dimethyl formamide [110], starch [111], pinacol [112–115], amines [116,117], alcohols [118–124,132–135], carboxylic acids [142–144], amino acids [150,151], thiourea [125–127], acetophenone [128], thiomalic acid [129], 2-mercaptoethanol [130], and triethyl borate [131] may be used.

Pramanick and Sankar [99] investigated the polymerization of methyl methacrylate polymerization initiated by only ceric ions and found that the mechanism of initiation depends strongly on the acidity of the medium and is independent of the nature of anion associated with the ceric ion. In a moderately acidic medium, the primary reaction is the formation of hydroxyl radical by ceric-ion oxidation of water. When ceric sulfate is used, the hydroxyl radicals initiate the polymerization and appear as end groups in the polymer molecule. If, on the other hand, ceric ammonium sulfate or a mixture of ceric sulfate and ammonium sulfate are used, some of the hydroxyl radicals react with the ammonium ion, producing ammonium radicals, and both radicals act as initiators, giving polymers with both hydroxyl and amino end groups. In the polymerization of acrylamide by ceric salt, the infrared (IR) spectra suggests the formation of monomer–ceric salt complexes in aqueous solution [98]. This coordination bond presumably consists of both

σ - and π -type bonds. It is likely that for acrylamide, the reaction mechanism is not of the redox type, but based on complex formation.

Various alcohols such as benzyl alcohol [124], ethanol [120], ethylene glycol [119], and 3-chloro-1-propanol [132] have been employed with ceric ions to form redox systems for homopolymerization or graft copolymerization. Regarding block copolymerization [136], the alcohol used is generally a dialcohol or multifunctional oligomeric or even a high-molecular-weight alcohol. A typical mechanism, based on the oxidation of a special, azo-containing polyethyleneglycol, is illustrated in Eq. (45) [133–135].



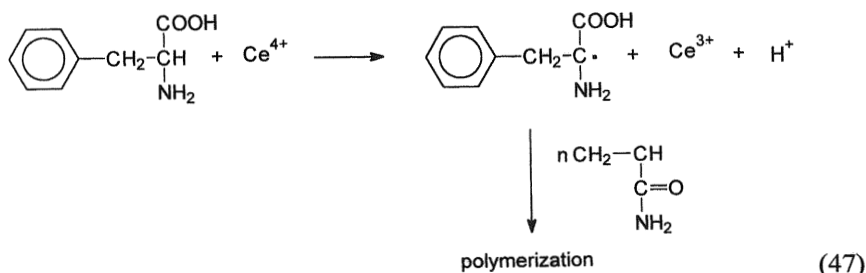
The mechanism depicted in Eqs. (45) and (46) involves the production of one proton and of oxygen-centered radicals, which initiate vinyl polymerization in the presence of the monomer. As a result, a polymer with one central azo bond is formed. When heated in the presence of a second monomer, this macro-initiator is split at the azo side, giving rise to two initiating macro-radicals [Eq. (46)]. The final result is tailor-made multiblock copolymers. Other hydroxyl-groups containing high-molecular-weight compounds used in conjunction with Ce(IV) salts include methyl cellulose and methyl hydroxypropyl cellulose [137].

In addition to alcohols, pyrroles have also been found to be suitable activators in the Ce(IV)-initiated polymerization. In some recent work, polypyrrole was synthesized by an oxidation of pyrrole with Ce(IV) [138,139].

The polymerization of acrylonitrile [116] by ceric ions was found to be accelerated by secondary and tertiary amines, but not by primary amines. This phenomenon may be due to the fact that the acceleration is due to a

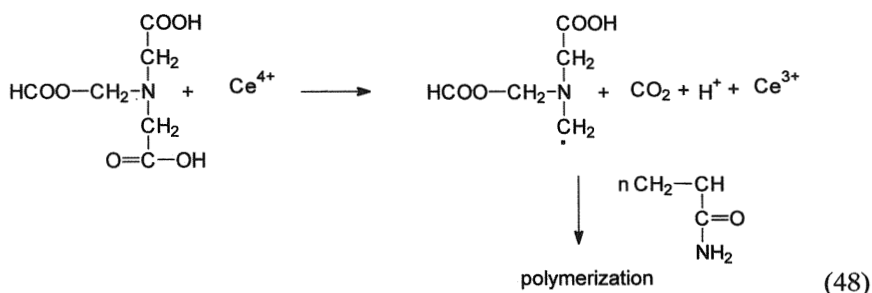
redox reaction between ceric ions and amines and, therefore, depends on the electron-donating ability of the substituents. The order of reactivity of amines is triethanolamine > triethylamine > diethanolamine > diethylamine. Pramanick [117] polymerized methyl methacrylate in the presence of $\text{Ce}(\text{ClO}_4)_4$ and monoamines and reported the formation of polymethyl methacrylate containing amine end groups. With ethanolamines, products containing reactive OH groups were obtained.

Various amino acids, such as serine, glucine, or phenylalanine, have been employed in conjunction with $\text{Ce}(\text{IV})$ for the radical polymerization or acrylamide [140,141]. Polymerizations were conducted in sulfuric acid solution. It was found that the resulting polymers contained carboxylic end groups. The mechanism of initiation is illustrated in the example of phenylalanine:



In the polymerization of acrylamide and of acrylonitrile, carboxylic acids also have been used in conjunction with $\text{Ce}(\text{IV})$ in diluted sulfuric acid solution [150–154]. The carboxylic acids that turned out to be useful in this respect include malonic acid, tartaric acid, and citric acid. In all cases, the polymers were found to be equipped with carboxylic end groups. In one work [145], polymerization and electrolysis were carried out simultaneously. This allows $\text{Ce}(\text{III})$ to be converted to $\text{Ce}(\text{IV})$ in the course of polymerization. The highest polymerization rates were obtained when stainless-steel electrodes were used for $\text{Ce}(\text{III})$ oxidation.

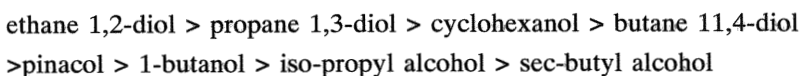
Another system for the polymerization of acrylamide are chelating polyaminocarboxylic acids with $\text{Ce}(\text{IV})$ [146–148]. In these systems, the redox reaction is followed by a decarboxylation to yield the initiating carbon-centered radical. It was found that diethylenetriamine pentaacetic acid (DTPA) is slightly more effective than ethylenediamine tetraacetic acid (EDTA). The efficiency of nitrilotriacetic acid (NDA) [see Eq. (48)] is smaller than that of EDTA.



3. Vanadium(V)

Vanadium(V) in the presence of various organic reducing agents has been used as an effective initiator in the polymerization of vinyl monomers [149]. In this redox system, the initiating radicals are also generated from the reducing agent by the decomposition of an intermediate complex formed between oxidant and reductant. Vanadium(V) with a large number of organic substrates, namely cyclohexanol [150–152], lactic [152] and tartaric acid [153], cyclohexanone [154], cyclohexane [155], ethylene glycol [156], thiourea, ethylene thiourea [157–159], and propane 1,2-diol [160], has been used in free-radical polymerization processes.

Based on the systematic investigation [156] of the V^{5+} /alcohol redox system for the polymerization of acrylonitrile, the order of the activity of the alcoholic compounds was found to be



A vanadium(V)-based redox system has been applied to grafting of vinyl monomers onto various polymeric substrates (Table 1). Besides graft copolymers, homopolymers were also formed.

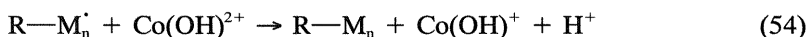
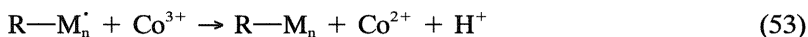
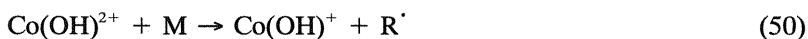
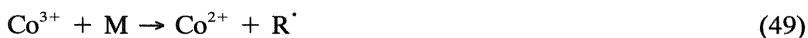
4. Cobalt(III)

Cobalt(II) invariably exists as an octahedrally coordinated ion, and has d electrons which can become involved both in electron transfer reaction and ligand bonding [164]. The powerful oxidizing capacity of trivalent cobalt has been shown by several investigators [165–183]. A wide variety of organic compounds—aromatic as well as aliphatic aldehydes, olefins, ketones, hydrocarbons, and alcohols—have been found to be susceptible to oxidation by cobaltic ions, and the kinetics of these reactions have been reported in detail. That Co^{3+} could initiate the vinyl polymerization was suggested by Baxendale et al. [184]. Later, Santappa and co-workers [185–187] investi-

Table 1 Grafting of Vinyl Monomers onto Polymers by Using Vanadium(V)-Based Redox System

Monomer	Trunk polymer	Ref.
Acrylonitrile	Collagen	161
Vinyl acetate	Collagen	161
Methyl methacrylate	Cellulose	162
Acrylonitrile	Dialdehyde cellulose	163
Acrylonitrile	Polymethacrolein	163
Vinyl pyridine	Polyacrylamide	163
Vinyl monomers	Wool	159

gated the polymerization of methyl methacrylate, methyl acrylate, acrylonitrile, and acrylamide initiated by a redox system involving Co^{3+} . From the experimental results, the following general mechanism was proposed:



Notably, cobaltic ions participate in both initiation and termination processes. These authors [188] also investigated the polymerization of methyl methacrylate initiated by Co^{3+} /*tert*-butyl alcohol and found that the redox system is operative only at high concentration. The cobaltous chloride/dimethyl aniline redox system for the polymerization of acrylamide was also reported [189].

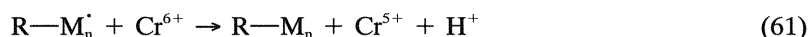
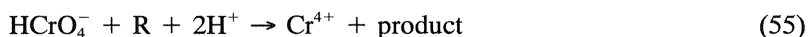
The aqueous polymerization of methyl methacrylate initiated by the potassium trioxalate cobaltate (II) complex was studied by Guha and Palit [190]. At a relatively higher concentration ($>0.001 \text{ mol L}^{-1}$), this compound can initiate aqueous polymerization of methyl methacrylate in the dark at room temperature. The complex is highly photosensitive, which can photoinitiate polymerization. A detailed end-group analysis of the obtained polymers indicated that carboxyl and hydroxyl radicals, which are from the decomposition of the photoexcited complex, are the initiating species.

5. Chromium(VI)

Chromic acid is one of the most versatile oxidizing agents [191]. Viswanathan and Santappa [192] investigated chromic acid/reducing agent (*n*-butanol, ethylene glycol, cyclohexanone, and acetaldehyde) initiated polymerization of acrylonitrile. These authors [193] also observed that the percentage of conversion to polymer was more with acrylonitrile monomer and much less with monomers such as methyl acrylate and acrylamide under similar experimental conditions. This difference of reactivities of monomers could be explained by assuming that Cr^{6+} species terminated the chain radicals more effectively with respect to the latter monomers than with polyacrylonitrile radicals.

The Cr^{6+} /1-propanol, Cr^{6+} /1,2-propane diol, Cr^{6+} /phenyl *tert*-butyl alcohol, Cr^{6+} /thiourea, and Cr^{6+} /ethylene thiourea systems have been studied in the polymerization of acrylonitrile [194,195]. These studies furnished information on polymerization kinetics and the general mechanism of chromic acid oxidations. The mechanism involves the formation of unstable species such as Cr^{6+} and Cr^{5+} .

The following reaction scheme involving the initiation by Cr^{4+} or R , and termination by Cr^{6+} , which was in line with the experimental results, was proposed:



Potassium chromate in conjunction with a variety of reducing agents was used to initiate emulsion copolymerization of styrene and butadiene [196]. Arsenic oxide was found to be the most powerful reducing agent. Here, again, the formation of unstable species Cr^{6+} and Cr^{5+} was responsible for the initiation.



The $\text{Cr}_2\text{O}_3/\text{NaHSO}_3$ redox system for the aqueous polymerization of

methyl methacrylate was also described [197]. Nayak et al. [198] reported grafting methyl methacrylate onto wool by using a hexavalent chromium ion. In this case, macroradicals were produced by reaction of Cr^{6+} with wool in the presence of perchloric acid.

6. Copper(II)

The Cu^{2+} /potassium disulfide [199] and Cu^{2+} /metabisulfide [200] redox systems have been used in the polymerization of acrylonitrile and acrylamide, respectively. The cupric sulfate–hydrazine redox system in which hydrazyl radicals are responsible for the initiation was studied in the absence and presence of molecular oxygen. The Cu^{2+} /hydrazine hydrate [201–204] and Cu^{2+} /2-aminoethanol [205] systems were used for the polymerization of vinyl monomers. Misra [206] demonstrated that the polymerization of acrylamide could be initiated by the Cu^{2+} /metabisulfide redox system. Initiating systems of cupric(II) ions in conjunction with dimethyl aniline [207] and α -amylase [208] were also reported. Cupric-ion-based redox reactions were successfully applied [209] to graft vinyl monomers onto wool and Nylon-6.

7. Iron(III)

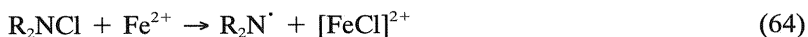
Bamford et al. [210] and Bengough et al. [211] reported that ferric salt acts as an electron transfer agent. Cavell et al. [212] showed that the rate of polymerization is proportional to the reciprocal of the concentration of the ferric salt. The role of ferric salt in the polymerization of acrylamide initiated by ceric salt was studied by Narita et al. [113].

The polymerization of methyl methacrylate in acidic solution by iron metal was reported earlier [213]. Palit and co-workers [214] studied the mechanism of methyl methacrylate in the presence of ferric chloride. They proposed that the hydroxyl radical formed by the chemical decomposition of the system containing ferric salt is the active species for initiating polymerization. Narita et al. reported [215] the polymerization of acrylamide initiated by ferric nitrate and suggested that a complex of monomer and metallic salt generates an active monomer radical capable of initiating vinyl polymerization.

The reaction between Fe^{3+} and monomercaptides was studied extensively [216–218]. It was shown that complexes formed between Fe^{3+} and monomercaptides such as thioglycolate or cysteinate invariably undergo redox reaction in which the monomercaptides oxidized to disulfide, and Fe^{3+} is reduced to Fe^{2+} . The formation of the intermediate thiol radical by the interaction of iron(III) with mercaptans, which can initiate vinyl polymerization, was reported by Wallace [219]. The Fe^{3+} /thiourea redox pair was investigated for the initiation of polymerization of methyl methacrylate, sty-

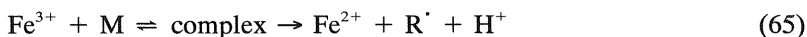
rene, and acrylonitrile by several research groups [220–227]. In general, the initiating species is formed by the abstraction of the hydrogen atom of the –SH group of the isothiurea form in the presence of the ferric ion. It was also found that the rate of polymerization was effected by the substitution of the amino group of the thiourea.

Brown et al. [228] reported the redox system of hydrazine and ferric ammonium sulfate for the polymerization of methyl methacrylate. *N*-haloamines in conjunction with Fe^{2+} were found [229] to be efficient redox initiators for the polymerization of methyl methacrylate. Amino radicals formed according to the following reaction initiate the polymerization:



The trimethyl amine oxide/ Fe^{2+} system in aqueous medium initiates the polymerization of methyl methacrylate in a similar electron transfer process [230]. Interestingly, acrylonitrile and acrylamide were not polymerizable with this system. On the other hand, acrylamide was polymerized by iron(III) with bisulfite [231] and 4,4'-azobis(cyanopentanoic acid) [232] redox couples.

Narita et al. [233] investigated the polymerization of methyl methacrylate in the presence of ferric nitrate. The ferric nitrate in dilute solutions was found to initiate the polymerization. At a comparatively higher concentration, the ferric salt reacts as an electron transfer agent, and the rate of polymerization is decreased with increasing concentration. The following reaction mechanism was proposed:



Fe^{3+} -induced redox reactions were used in grafting methyl methacrylate onto cellulose [234] and acrylonitrile and acrylamide onto polyamides such as Nylon 6,6 and 6,10 [235].

D. Initiation by Permanganate-Containing Systems

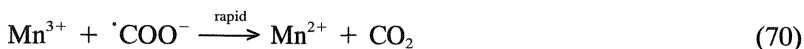
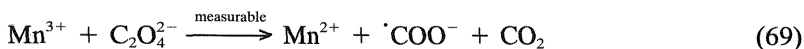
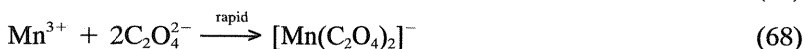
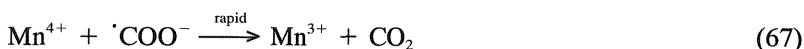
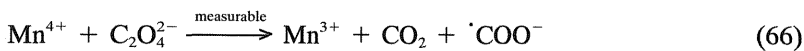
The permanganate ion is known [236] to be a versatile oxidizing agent, because of its ability to react with almost all types of organic substrates. Its reaction is most interesting because of the several oxidation states to which it can be reduced, the fate of manganese ion being largely determined by the reaction conditions; in particular, the acidity of the medium. Considerable work has been done in elucidating the mechanism of permanganate oxidations of both organic and inorganic substrates and many of these are well understood. The permanganate ion coupled with simple water-soluble organic compounds act as an efficient redox system for the initiation of vinyl polymerization.

Palit and co-workers [237,238] used a large number of redox initiators containing permanganate as the oxidizing agent. The reducing agents are oxalic acid, citric acid, tartaric acid, isobutyric acid, glycerol, bisulfite (in the presence of dilute H_2SO_4), hydrosulfite (in the presence of dilute H_2SO_4), and so forth. The peculiarity of the permanganate system is that there are two consecutive redox systems in the presence of monomer:

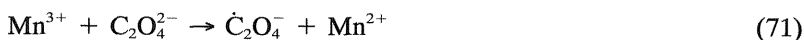
1. The monomer (reductant) and permanganate (oxidant)
2. Added reducing agent (reductant) and separated manganese dioxide (oxidant)

Konar and Palit [239] studied the aqueous polymerization of acrylonitrile and methyl methacrylate initiated by the permanganate oxalic acid redox system. The rate of polymerization is independent over a small range. The molecular weight of polymers is independent of oxalic acid concentration in the range where the rate of polymerization is independent of the oxalic acid concentration. However, the molecular weight decreased at a higher concentration of oxalic acid with an increasing concentration of catalyst and temperature. The addition of salts, such as Na_2SO_4 , and complexing agents, such as fluoride ions and ethylene diaminetetracetic acid, decreased the rate of polymerization, whereas the addition of detergents and salts, such as MnSO_4 , at low concentrations increased the rate.

Weiss [240] reported the activation of oxalic acid and observed that it acquires an increased reducing power when treated with an insufficient amount of an oxidizing agent (KMnO_4). The action of KMnO_4 on oxalic acid at room temperature is a relatively slow process which occurs in steps. A possible mechanism was given by Launer and Yost [241] for the generation of carboxyl radicals ($\text{C}_2\text{O}_4^{\cdot-}$ or $\text{COO}^{\cdot-}$), which appear to be the initiating radicals in this system:



Weiss [240] suggested that the continuous production of active oxalic acid ion radical ($\text{C}_2\text{O}_4^{\cdot-}$) in this system is governed by the reaction



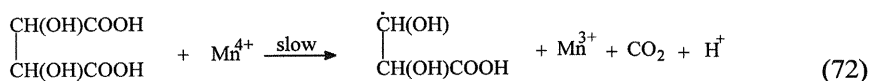
At room temperature, this active oxalic acid ion radical has a life of about $\frac{1}{2}$ hr. Therefore, the system behaves in such a manner that the aqueous polymerization caused by the reaction of monomer with carboxyl radicals tends toward its completion within $\frac{1}{2}$ hr or so after initiation.

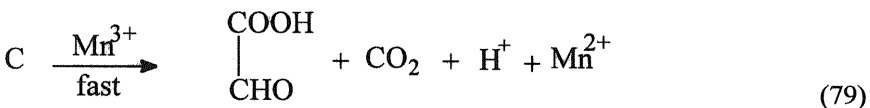
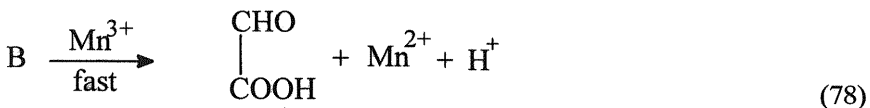
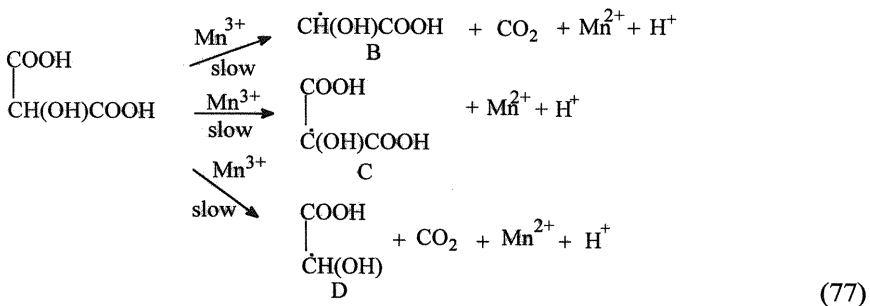
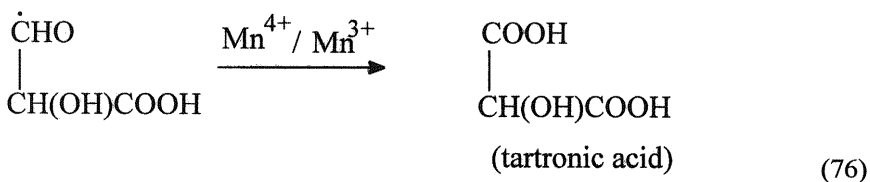
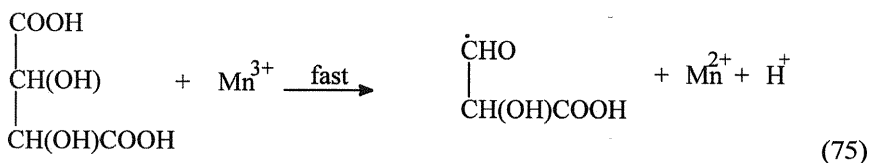
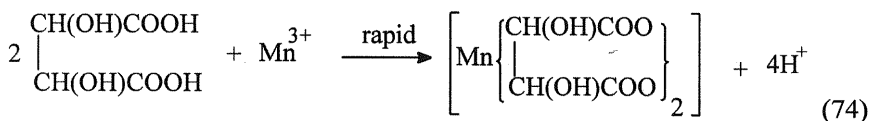
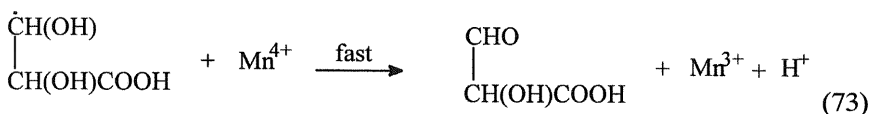
The aqueous polymerization of acrylic acid, methacrylic acid, acrylamide, and methacrylamide using potassium permanganate coupled with a large number of organic substrates as the reducing agent was studied by Misra et al. [242–246]. The rate of polymerization of acrylic and methacrylic acid initiated by the permanganate/oxalic acid redox system was investigated in the presence of certain neutral salts and water-soluble organic solvents, all of which depress the rate of polymerization, whereas Mn^{2+} ions have been found to increase the initial rate but to depress the maximum conversion [242].

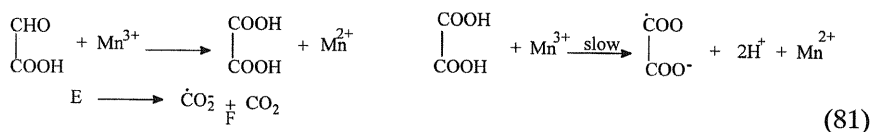
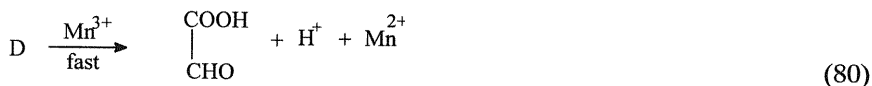
The rate of acrylamide polymerization initiated by the permanganate/tartaric acid [245] and the permanganate/citric acid [246] redox system increasing with increasing catalyst and monomer concentration. The initial rate increased with increasing temperature, but the conversion decreased beyond 35°C . The addition of neutral salts like $\text{Co}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$, organic solvents, and complexing agents reduced the rate and percentage of conversion. However, the addition of MnSO_4 or the injection of more catalyst at intermediate stages increased both initial rate and the maximum conversion.

The redox reaction of tartaric acid and manganic pyrophosphate was studied by Levesley and Waters [247]. They suggested the formation of a cyclic complex between the two components that dissociate with loss of carbon dioxide and formation of free-radical $\dot{\text{C}}\text{H}(\text{OH})$, capable of initiating vinyl polymerization. The distinguishing feature of the permanganate system is that there are two consecutive redox systems operative in the presence of the monomer [i.e., permanganate (oxidant) and monomer (reductant); and separated manganese dioxide (oxidant) and the added reducing agent (reductant)].

In the aqueous polymerization of acrylamide initiated by the permanganate/tartaric acid system, the permanganate first reacts with tartaric acid to generate the highly reactive Mn^{3+} ions and the active free radical, capable of initiating the polymerization. The detailed mechanism of the latter reaction could be presented by Eqs. (72)–(81):



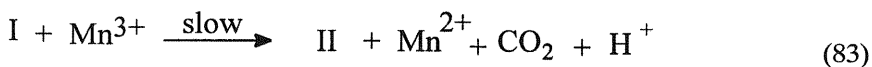
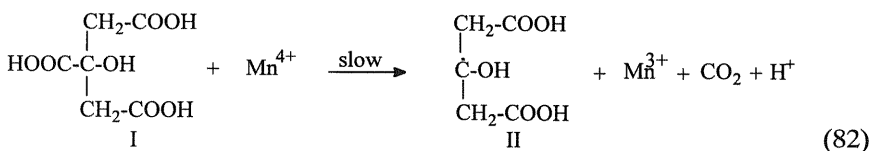




The free radicals A, B, C, EE, and F are all capable of initiating the polymerization of acrylamide.

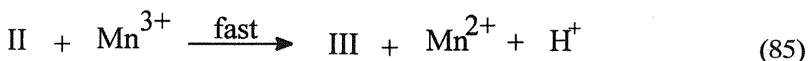
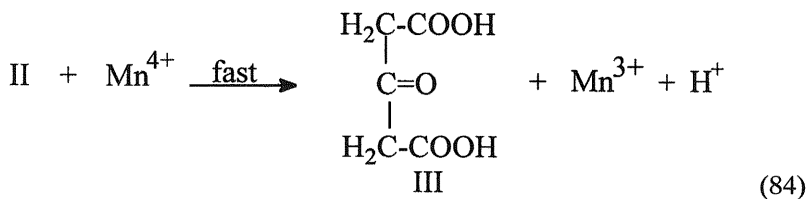
In the case of acrylamide polymerization initiated by the citric acid/perpermanganate system, the oxidation of citric acid leads to a keto-dicarboxylic acid, which, upon drastic oxidation, transformed into acetone and carbon dioxide [246]. The mechanism of the redox system is as follows:

At low concentration of KMnO_4 :



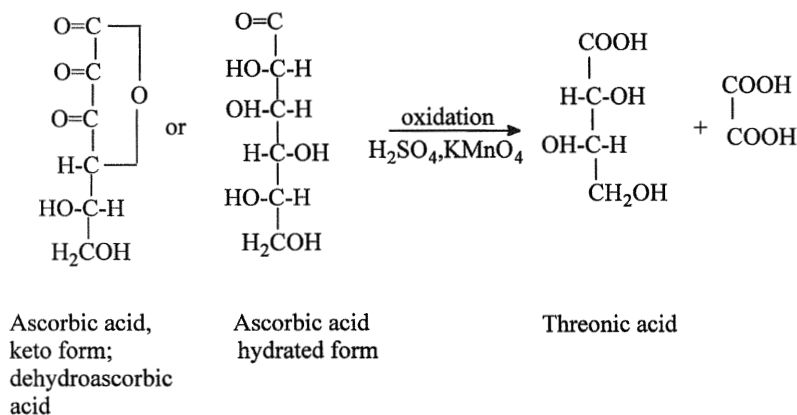
The free radicals II initiate polymerization and the reaction [Eq. (82)] is the main rate-determining step.

At high concentrations of KMnO_4 :



Shukla and Mishra [248] studied the aqueous polymerization of acrylamide initiated by the potassium permanganate/ascorbic acid redox system. Ascorbic acid has been used in a reducing agent with several oxidants (i.e., H_2O_2 [249], $\text{K}_2\text{S}_2\text{O}_8$ [250], and *tert*-butyl peroxybenzoate [251]) to produce free radicals capable of initiating polymerization in the aqueous media. The initial rate of polymerization was proportional to the first power of the oxidant and monomer concentration and independent of ascorbic acid concentration in the lower concentration range. At higher concentrations of ascorbic acid, the rate of polymerization and the maximum conversion decreased as the temperature was increased from 20°C to 35°C . The overall activation energy was $10.8 \text{ kcal mol}^{-1}$. The rate of polymerization decreased by the addition of water-miscible organic solvents or salts such as methyl alcohol, ethyl alcohol, isopropyl alcohol, potassium chloride, and sodium sulfate, whereas the rate increased by the addition of Mn^{2+} salts and complexing agents such as NaF.

Permanganate oxidizes ascorbic acid to form threonic acid and oxalic acid as presented below. The permanganate reacts with oxalic acid to produce the $\cdot\text{COO}^-$ radical which initiates polymerization.



(86)

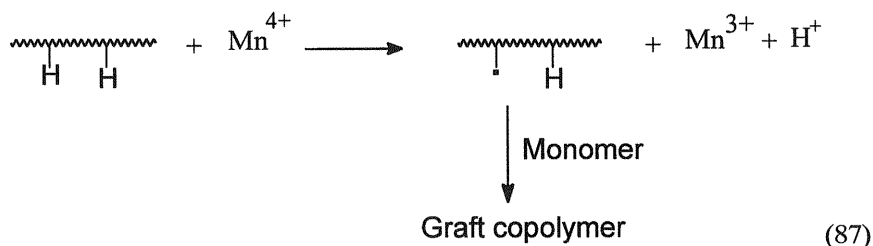
The effect of some additives on aqueous polymerization of acrylamide initiated by the permanganate/oxalic acid redox system was studied by Husain and Gupta [252]. The rate of polymerization was increased in the presence of alkali metal chlorides. However, the rate was decreased in the presence of cupric chloride and ferric chloride. Anionic and cationic detergents showed a marked influence on the rate of polymerization.

Permanganate based redox systems were used to graft vinyl monomers onto various natural and synthetic polymers (Table 2). In these systems, macroradicals were formed by a redox reaction between the manganese(IV)

Table 2 Grafting of Vinyl Monomers onto Polymers by Using Permanganate-Based Redox System

Monomer	Trunk polymer	Redox system	Ref.
Methyl methacrylate	Silk	KMnO ₄ –H ₂ SO ₄	253
Methyl methacrylate	Silk	KMnO ₄ –oxalic acid	254
Methyl methacrylate	Nylon-6	KMnO ₄ –various acids	255, 256
Acrylonitrile	Nylon-6	KMnO ₄ –various acids	255, 256
Acrylic acid	Nylon-6	KMnO ₄ –various acids	255, 256
Butyl methacrylate	Cellulose	KMnO ₄	257
Acrylonitrile	Starch	KMnO ₄	258

ion and the polymer to be grafted, according to the following general reaction:



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6

Suspension Polymerization Redox Initiators

Munmaya K. Mishra, Norman G. Gaylord, and Yusuf Yagci

I. INTRODUCTION

The conditions under which radical polymerizations are carried out are both of the homogeneous and heterogeneous types. This classification is usually based on whether the initial reaction mixture is homogeneous or heterogeneous. Some homogeneous systems may become heterogeneous as polymerization proceeds due to insolubility of the polymer in the reaction media. Heterogeneous polymerization is extensively used as a means to control the thermal and viscosity problems. There are three types of heterogeneous polymerization: precipitation, suspension, and dispersion.

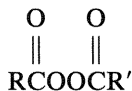
The term suspension polymerization (also referred to as bead or pearl polymerization) refers to polymerization in an aqueous system with a monomer as a dispersed phase, resulting in a polymer as a dispersed solid phase. The suspension polymerization is carried out by suspending the monomer as droplets (0.001–1 cm in diameter) in water (continuous phase). In a typical suspension polymerization, the initiator is dissolved in the monomer phase. Such initiators are often referred to as oil-soluble initiators. Each monomer droplet in a suspension is considered to be a small bulk polymerization system and the kinetics is the same as that of bulk polymerization. The suspension of a monomer is maintained by agitation and the use of stabilizers. The suspension polymerization method is not used with mono-

mers which are highly soluble in water or whose polymer has too high a glass transition temperature. The method is used commercially to prepare vinyl polymers such as polystyrene, poly(methyl methacrylate), poly(vinyl chloride), poly(vinyl acetate), poly(vinylidene chloride), and poly(acrylonitrile). Various types of redox initiator are used to prepare such polymers by suspension polymerization. The following examples describe the various types of initiating system for suspension polymerization.

Suspension polymerization is essentially equivalent to bulk polymerization but is carried out in a reaction medium in which the monomer is insoluble and dispersed as a discrete phase (e.g., droplets), with a catalyst system that generates or permits the entry of radical species within the suspended monomer phase or droplets. The following review presents examples of initiators for bulk polymerization as well as suspension polymerization, as initiating systems suitable for bulk polymerization due to monomer-soluble catalysts are potentially useful in suspension polymerization.

II. ACYL PEROXIDE

Acyl peroxides may be defined as substances of the type



where R and R' are either alkyl or aryl. Acyl peroxides have been one of the most frequently used sources of free radicals, and interest in their various modes of decomposition has been keen. Acyl peroxides [i.e., benzoyl peroxide (Bz_2O_2) and lauroyl peroxide (LPO)] have been used extensively as the initiator for suspension polymerization of styrene [1–4], vinyl chloride [5–7], and vinyl acetate [8].

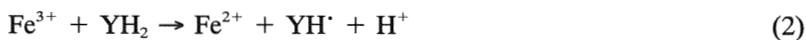
A. Fe^{2+} as Reductant

Kern and other investigators [9,10] found Bz_2O_2 to be very effective in both aqueous and nonaqueous media with or without heavy metals as a component. Kern [9] based his theory of reaction on Haber's earlier suggestions and formulated the production of radicals as an electron transfer process. He proposed a Haber–Weiss type of mechanism for two-component systems:



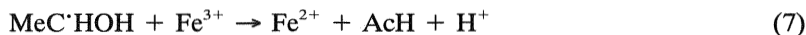
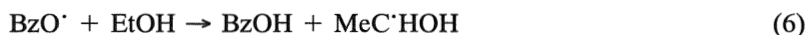
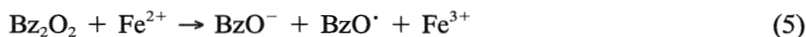
where RCOO^\cdot is the active species.

In the presence of a third component, a reducing agent (YH_2), the reaction continues as follows:

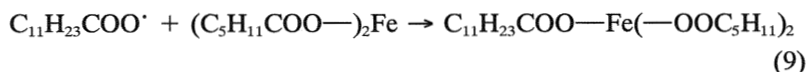
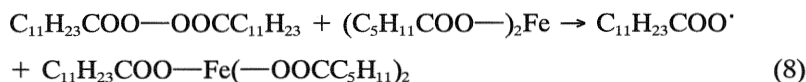


etc.

The effect of activators like FeSO_4 [11,12] for emulsion polymerization and ferric stearate [13] for bulk polymerization of vinyl monomers in combination with acyl peroxide has been studied. The ferrous ion catalyzed decomposition of Bz_2O_2 in ethanol has been studied in some detail by Hasegawa and co-workers [14,15]. The cycle, which requires reduction of Fe^{3+} by solvent-derived radicals, yields a steady-state concentration of Fe^{2+} after a few minutes, shown spectroscopically to be proportional to the initial concentration of the ferrous ion [14]. The second-order rate constant for the following reaction was found to be $8.4 \text{ L mol}^{-1} \text{ sec}^{-1}$ at 25°C , with an activation energy of $14.2 \text{ kcal mol}^{-1}$:



The suspension polymerization of vinyl chloride using lauroyl peroxide (LPO) and a water-soluble Fe^{2+} salt [16,17] and monomer-soluble [18–20] Fe^{2+} salt as the reducing agent has been studied. In the case of a monomer-soluble reducing agent like ferrous caproate, the mechanism of initiation of the polymerization is considered to be an one-electron transfer reaction in the monomer phase as follows:



Das and Krishnan [21] had reported the suspension polymerization of vinyl acetate and vinyl alcohol using a redox pair of Bz_2O_2 and ferrous octoate (reducing agent). A high degree of polymerization was achieved using this redox-pair-initiating system.

Suspension Polymerization of Vinyl Chloride

In the suspension polymerization of vinyl chloride using LPO and a water-soluble reducing agent [16,17], $\text{Fe}(\text{OH})_2$ (produced by in situ reaction of a ferrous salt and an alkali metal hydroxide), the conversion was 80% and 65% by using a Na maleate–styrene copolymer and poly(vinyl alcohol) as the dispersing agent, respectively. The reaction was carried out according to the recipe presented in Table 1.

The suspension polymerization of vinyl chloride was also carried out at -15°C using a monomer-soluble reducing agent like ferrous caproate [18,19]. The molecular weight of the poly(vinyl chloride) decreased as the concentration of the iron(II) system increased, because of chain termination reactions. Konishi and Nambu [20] also reported low-temperature polymerization of vinyl chloride using the LPO–ferrous caproate redox system. The reaction was studied by varying the temperature from -30°C to $+30^\circ\text{C}$ with a molar ratio of oxidant to reductant of 1:1. The activation energy of the overall rate of polymerization was $6.5 \text{ kcal mol}^{-1}$. The initial rate increased, and the degree of polymerization decreased, with increasing ratio of ferrous caproate to LPO. The relative efficiencies of the peroxide with the reducing agent ferrous caproate were measured and are presented in Table 2.

A moderate rate of polymerization and a maximum yield were obtained by appropriate, continuous charging of the catalyst ingredients rather than the one-time addition. The syndiotacticity was increased as the polymerization temperature decreased. The initial rate was increased with the increasing ratio of ferrous caproate to LPO, but after passing through the ratio of unity, the maximum yield of the polymer suddenly became lower. This could be attributed to the decrease in the number of initiating radicals as shown in reaction (9). The oxidation–reduction reaction initiates and the polymerization can proceed readily in the monomer phase by using a monomer-soluble reducing agent.

Table 1 Typical Recipe: Suspension Polymerization of Vinyl Chloride^a

Ingredients	Amount (ppm)
0.03% Aqueous dispersing agent	200
FeSO_4	0.15
Vinyl chloride	100
Lauroyl peroxide	0.2
$\text{HCCl}=\text{CCl}_2$	40
0.5% Aqueous NaOH	1.7

^aPolymerization for 5 hr at 20°C .

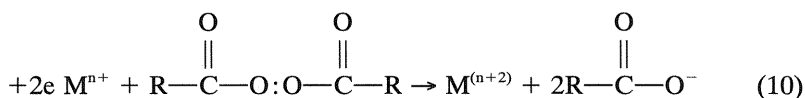
Table 2 Relative Efficiency of the Peroxides

Peroxides	Temp. (°C)	Rate of polymerization (% hr)
Lauroyl peroxide	-15	4.5
2,4-Dichlorobenzoyl peroxide	-15	1.5
Benzoyl peroxide	-15	1.4
Cumene hydroperoxide	-15	0.8
Di- <i>tert</i> -butyl hydroperoxide	-15	0.7

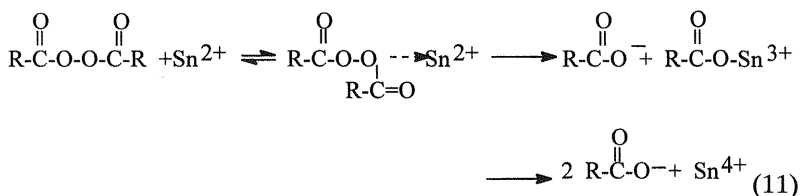
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B. Sn^{2+} as Reductant

Organic peroxides may decompose in a number of different ways when treated with ions of variable oxidation number. The reaction can be rationalized on the basis of the following general reaction:



The reaction of diacyl peroxide with stannous chloride in acid solution in room temperature or at a slightly elevated temperature is used in the quantitative analysis of the peroxygen compounds [22]. The reaction of the peroxygen compound with stannous chloride in the acid medium is apparently rapid and complete enough at room temperature to serve as a quantitative assay method. However, there is no information as to the nature of the decomposition products (i.e., radical or ionic). In the absence of other evidence, the most reasonable mechanism would appear to be a heterolytic process as shown in reaction (11):



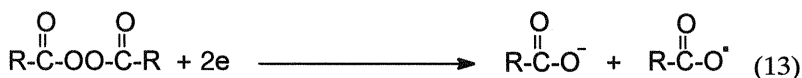
There is some evidence of the free-radical mechanism of polymerization using a peroxygen compound and Sn^{2+} halides. The effective polymerization of vinyl chloride in the presence of the peroxyester- SnCl_2 catalyst system confirms the generation of free radicals [23]. This contrasts with the reported rapid decomposition of diacyl peroxides in solution at

room temperature in the presence of various metal halides, to nonradical species through ionic intermediates. Thus, a polar carbonyl inversion mechanism is proposed in the decomposition of benzoyl peroxide and/or other diacyl peroxide in the presence of aluminum chloride [24–27], antimony pentachloride [26–28], and boron trifluoride [25–27].

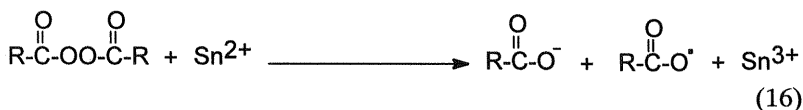
However, radical generation has been confirmed in the polymerization of various monomers in the presence of a catalyst system consisting of an aluminum alkyl and either a diacyl peroxide or a peroxyester (i.e., peroxygen compounds containing carbonyl groups) [29–31]. The proposed mechanism of decomposition involves complexation of the AlR_3 with the carbonyl group of the peroxide as well as with the monomer, resulting in an electron shift which weakens the peroxy linkage:



Although this mechanism may be operative to some extent, a redox mechanism analogous to that normally invoked in redox catalyst systems containing a peroxygen compound for the initiation of polymerization, considered to be a two-electron transfer reaction, probably plays a major role:

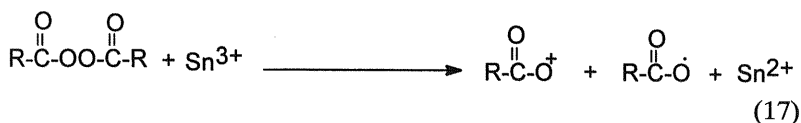


Another, a one-electron, transfer mechanism may be suggested for the formation of free radicals as follows:

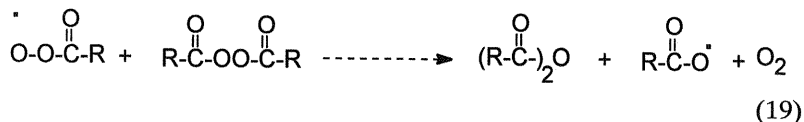


As Sn^{3+} is very unstable after formation, it may undergo reaction in

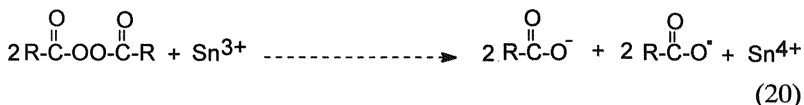
two ways in which it may again be reduced to Sn^{2+} or oxidized to a Sn^{4+} state. The reactions are as follows:



The $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{O}^{\bullet}$ radical, reaction (16), and $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}^{\bullet}$ radical, reaction (17), may react with acyl peroxide as follows:



or, in the other step, Sn^{3+} produced in reaction (16) may be oxidized to the Sn^{4+} state as follows:



The mechanism of polymerization may be represented as follows:

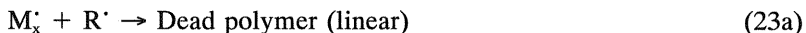
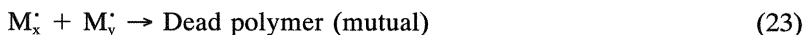
Initiation



Propagation



Termination



where M is the monomer, R^{\bullet} is the initiating radical, and k_i and k_p are the rate constants.

Table 3 Typical Recipe: Suspension Copolymerization of Acrylonitrile and Methyl Acrylate^a

Ingredients	Amount (ppm)
Water	200
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	0.02
75:25 Acrylonitrile–methyl acrylate	250
Dilauroyl peroxide	0.5
$\text{HCCl}=\text{CCl}_2$	40
0.5% Aqueous NaOH	1.7

^aPolymerization for 1 hr at 25°C followed by 15 hr at 60°C at stirring rate of 1000 rpm.

Suspension Copolymerization of Acrylonitrile with Methyl Acrylate and with Styrene

Kido et al. reported the suspension copolymerization of acrylonitrile–methyl acrylate [32] and acrylonitrile–styrene [33] using dilauroyl peroxide and the SnCl_2 redox system.

In the case of suspension copolymerization of acrylonitrile and methyl acrylate, mixtures of 40–85% acrylonitrile and 15–60% methyl acrylate were polymerized in an H_2O suspension using inorganic dispersants accord-

Table 4 Typical Recipe: Suspension Copolymerization of Acrylonitrile and Styrene^a

Ingredients	Amount (ppm)
Water	150
Hydroxylapatite	2
Polyethylene glycol alkyl aryl ether phosphate	0.01
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	0.02
Acrylonitrile	25
Styrene	75
<i>tert</i> -Dodecyl mercaptan	0.5
Dilauroyl peroxide	0.71
$\text{HCCl}=\text{CCl}_2$	40

^aPolymerization for 1 hr at 25°C followed by 15 hr at 60°C at stirring rate of 400 rpm.

ing to the typical recipe presented in Table 3 to produce 100- μ spherical copolymer beads.

In the case of suspension copolymerization of acrylonitrile–styrene mixtures of 10–40 wt% acrylonitrile and 40–90 wt% styrene are polymerized in H_2O in the presence of inorganic dispersing agents according to the typical recipe presented in Table 4 to produce transparent copolymer beads containing >90% 100–400- μ mesh particles.

C. Cu^{2+} as Reductant: Suspension Polymerization of Vinyl Chloride

Recently, Cozens [34] has reported the suspension polymerization of vinyl chloride using a $LPO-Cu^{2+}$ metal chelate redox pair system. The suspension polymerization of vinyl chloride [35] was also studied using a diacyl peroxide such as $Bz_2O_2-Cu^{2+}$ as the redox initiator. The microsuspension polymerization of vinyl chloride was carried out at 40–60°C. The conversion of 85% was obtained after 10 hr of polymerization according to the typical recipe presented in Table 5.

D. Tertiary Amines as Reductant

The use of tertiary amines as cocatalysts with metal ions in aqueous polymerization has been the subject of study of various workers [36]. No nucleophilic displacement in peroxidic oxygen has received more attention than that by amines [37]. Extensive studies with acyl peroxide were carried out by several workers [38–51].

The amine–peroxide combination as an initiator for vinyl polymerization has been investigated extensively by various workers. Solution polymerization of vinyl chloride [52] and styrene and methyl methacrylate [53], bulk polymerization of styrene [54], and dead-end polymerization of

Table 5 Typical Recipe: Suspension Polymerization of Vinyl Chloride^a

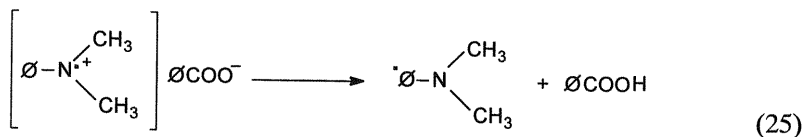
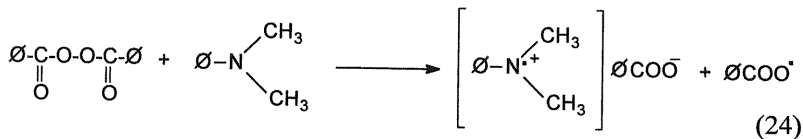
Ingredients	Amount (g)
Water	700
Vinyl chloride	675
Benzoyl peroxide	0.675
$CuSO_4 \cdot 5H_2O$	45 mg

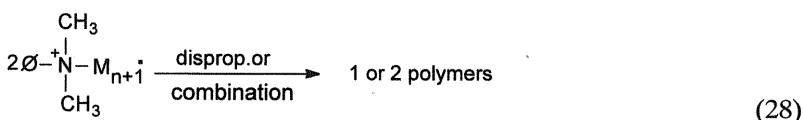
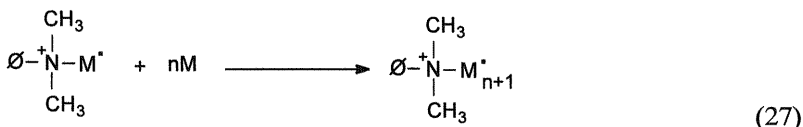
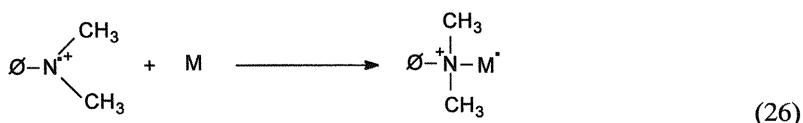
^aPolymerization for 10 hr at 50°C.

styrene and methyl methacrylate [55] were carried out using the benzoyl peroxide–dimethylaniline initiating system. Lal and Green [56] have reported the effect of various amine accelerators on the bulk polymerization of methyl methacrylate with benzoyl peroxide. At about the same time, Imoto and Takemoto [57] had reported the solution polymerization of acrylonitrile in the presence of a substituted benzoyl peroxide–dimethylaniline redox system. In another article, Takemoto et al. [58] have reported the solution polymerization of styrene using benzoyl peroxide and various di-n-alkylaniline redox systems. In a series of articles, O'Driscoll et al. reported on the bulk polymerization of styrene at 0°C [59] and higher temperatures [60] using benzoyl peroxide–dimethylaniline, and the bulk polymerization of styrene [61] using substituted diethylaniline and benzoyl peroxide. The efficiencies of free-radical production by various substituted benzoyl peroxides and substituted di-n-alkylanilines have also been studied [59–65]. Recently, the feasibility of the triethylamine–benzoyl peroxide [55] redox system to induce photopolymerization in solution has been reported.

The presence of free radicals in the reaction of tertiary amines and benzoyl peroxide has been observed by electron spin resonance (ESR) spectroscopy [67–69]. The reaction of amines with acyl peroxide is much more rapid than the thermal decomposition of the peroxide alone [70]. For example, benzoyl peroxide [53] with dimethylaniline at 0°C in styrene or chloroform exhibits an apparent second-order rate constant of $2.3 \times 10^{-4} \text{ sec}^{-1}$. However, acetyl [41] and lauroyl peroxide [71,72] react somewhat slower.

Recently, Morsi et al. [73] have studied the rate of charge transfer interactions in the decomposition of organic peroxides. O'Driscoll and Richezza [74] have also reported the ultraviolet absorbance study of the complex formation between benzoyl peroxide and dimethylaniline. According to Horner and Schwenk [45], the mechanism for the polymerization of vinyl monomers by benzoyl peroxide and dimethylaniline is as follows:



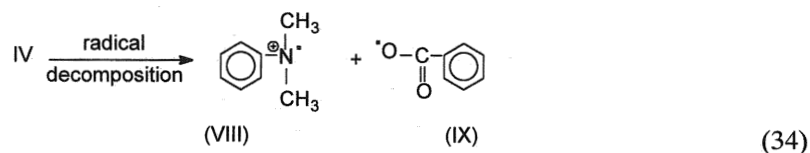
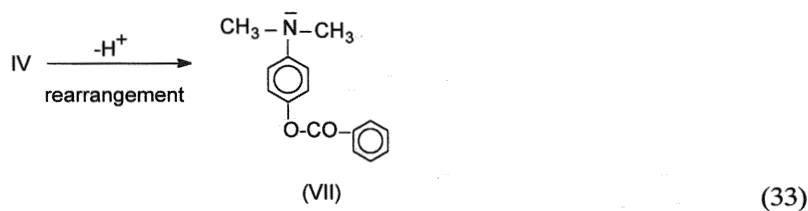
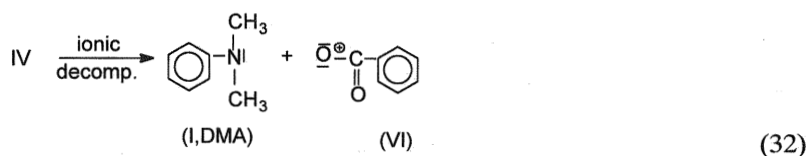
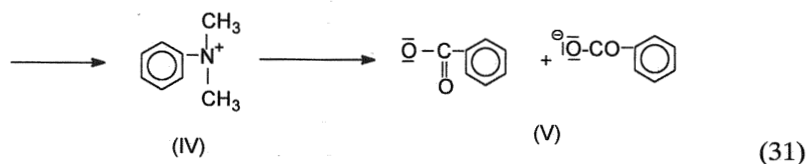
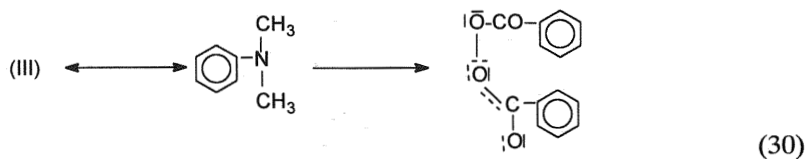
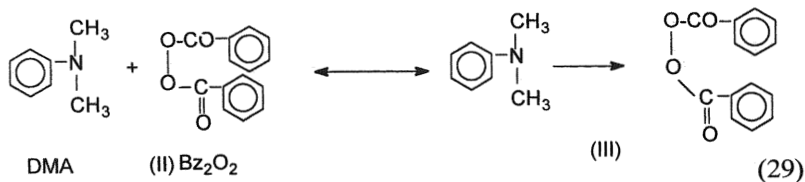


where steps (24) and (25) represent the formation of free radicals, step (26) the initiation of the monomer, step (27) the chain propagation, and step (28) the termination by combination or disproportionation.

They suggested that the dimethylaniline radical is the initiator. However, the mechanism was later questioned by Imoto et al. [52]. They suggested that the active radical (benzoate radical) produced by the interaction between benzoyl peroxide and dimethylaniline initiates the vinyl chloride polymerization.

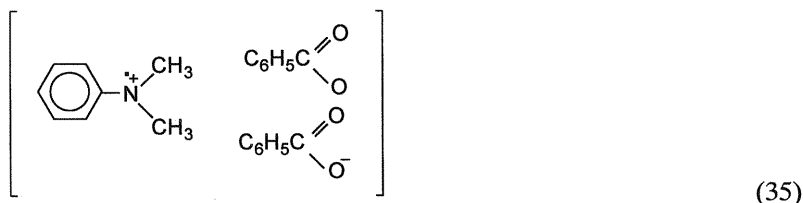
In a later study, Horner [38] postulated the detailed reaction mechanism of tertiary amine with benzoyl peroxide and pictured the initiation of polymerization by benzoate radical. Mechanistically speaking, the first stage of the amine-peroxide reaction is, unquestionably, nucleophilic attack on the O-O bond. Imoto and Choe [75] have studied the detailed aspects of the mechanism of the reaction between substituted benzoyl peroxide in the presence of dimethylaniline (DMA). The mechanism of the reaction of Bz_2O_2 with substituted dimethylaniline was studied by Horner et al. [44,45]. They have indicated that the higher the electron density of the lone pair on the nitrogen atom of substituted dimethylaniline, the stronger the promoting effect of the amine on the decomposition rate of Bz_2O_2 . It was shown that the more abundant the quantity of DMA, the faster the decomposition velocity of Bz_2O_2 .

In their study, Imoto and Choe [75] suggested the reversible formation of a complex intermediate III which subsequently decomposes into free radicals as follows:

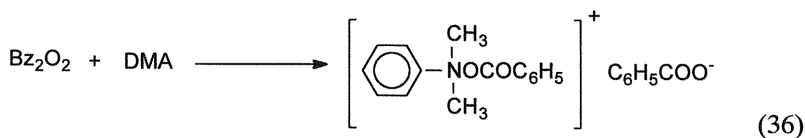


Although it seems clear that Bz_2O_2 and DMA undergo a bimolecular reaction giving rise to free radicals, the exact nature of the process is controversial. Thus, Horner [38] has proposed the formation of a "complex"

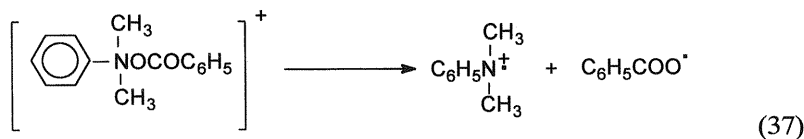
(35) as the rate-determining step, which subsequently gives rise to the observed products.

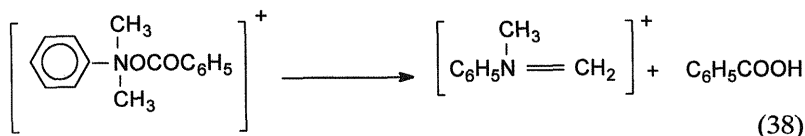


Imoto and Choe [75] have suggested the reversible formation of a complex, which subsequently decomposes into free radicals. But, Walling and Indictor [53] have suggested a new approach toward the free-radical mechanism between benzoyl peroxide and dimethylamine. They suggested that the rate-controlling step is a nucleophilic displacement on the peroxide by DMA to yield a quarternary hydroxylamine derivative. The reaction is as follows:

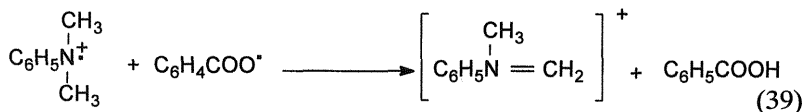


Such a formulation parallels that proposed for the bimolecular reaction [76] of peroxides and phenols, and, as it leads to an ionic product, should have a considerable negative entropy of activation. As has been pointed out previously [77], it also accounts for the accelerating effects of electron-supplying groups on the amine and electron-withdrawing groups on the peroxide, and parallels a plausible formulation of three other reactions: the reaction of peroxides with secondary amines, the formation of amine oxides in the presence of hydrogen peroxides, and the initiation of polymerization by amine oxides in the presence of acylating agents [78]. The product of reaction (36) has only a transient existence and decomposes by at least two possible paths:





Reaction (37), which gives Horner's [38] intermediate, represents a free-radical path and would account for the initiation of polymerization. As no significant amount of nitrogen is found in the resulting polymers, the amine fragment may well disappear by reacting with peroxide. Reaction (38) represents a nonradical breakdown and would account for the low efficiency of the system as a polymerization initiator. Admittedly, the same products could arise from a radical disproportionation closer to that suggested by Horner, but in the latter case, the reaction would have to occur in the same solvent "cage" as reaction (37), because otherwise, reaction (39) would compete with the initiation of polymerization and the efficiency of the latter would not show the independence of Bz_2O_2 and DMA concentration actually observed.



1. Suspension Polymerization of Vinyl Chloride

There was no induction period in the solution polymerization of vinyl chloride [52] initiated by the benzoyl peroxide–dimethylaniline system in various solvents such as tetrahydrofuran, ethylene dichloride, dioxane, cyclohexanone, methylethyl ketone, and so forth. The initial rate of polymerization and the conversion was directly and inversely proportional to the temperature, respectively. The polymerization was restricted to only 20% conversion, probably due to the complete consumption of benzoyl peroxide. Without the monomer, the extent of decomposition on benzoyl peroxide reaches a constant value regardless of the temperature and amount of dimethylaniline. It was seen that the greater the amount of dimethylaniline, the faster the initial rate of polymerization and the lower the conversion. The degree of polymerization of vinyl chloride obtained by the redox system benzoyl peroxide–dimethylaniline was generally lower than the polymer obtained by the benzoyl peroxide system alone. The activation energy of the polymerization by the redox system was lower than that of the benzoyl peroxide alone initiated polymerization and found to be $12.5 \text{ kcal mol}^{-1}$. The initial rate of polymerization could be expressed as

Table 6 Solution Polymerization of Vinyl Chloride in Tetrahydrofuran; $\text{Bz}_2\text{O}_2 = 0.52 \text{ mol } (\%)$

DMA Bz_2O_2	Temp. (°C)	Initial rate (%/min)	Maximum conversion (%)	DP
0.16	50	0.430	11.5	75
1.00	50	0.509	9.5	110
1.20	50	0.500	8.6	70
1.61	50	0.590	7.8	—
0.80	20	0.037	>26	85
0.80	30	0.120	<25	—
0.80	40	0.200	20.5	60
0.80	50	0.400	17.5	75
0.80	60	0.600	15.5	—

Source: Ref. 52.

$$\left(\frac{d(\text{PVC})}{dt} \right)_{t \rightarrow 0} = k(\text{Bz}_2\text{O}_2)^{1/2}(\text{DMA})^{1/2} \quad (40)$$

The results in the solution polymerization of vinyl chloride are summarized in Table 6.

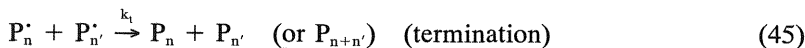
2. Suspension Polymerization of Acrylonitrile

Acrylonitrile. The solution polymerization of acrylonitrile [57] has been studied in benzene at 40°C by a dilatometer using dimethylaniline and various substituted benzoyl peroxide. It was found that the initial rate of polymerization increased with increasing the molar ratio of $\text{DMA}/\text{Bz}_2\text{O}_2$ from 0 to 5 by keeping the Bz_2O_2 concentration at $5.57 \times 10^{-5} \text{ mol L}^{-1}$. On the other hand, after a considerable polymerization time has elapsed, the polymer yields in the presence of a large quantity of DMA frequently became smaller than the yield obtained in the presence of smaller quantity of DMA. The relation between the initial rates of polymerization R_p^0 , and concentration of Bz_2O_2 and DMA may be expressed as

$$R_p^0 = k(\text{Bz}_2\text{O}_2)^{1/2}(\text{DMA})^{1/2} \quad (41)$$

The initial rate was also found to be directly proportional to the monomer concentration. On the basis of the kinetic data, a rate equation may be derived as follows:





Introduction of the steady state leads to

$$R = k_p(P_n^\cdot)(M) = k_p \left(\frac{k_i(M)}{k_t} \right)^{1/2} (BzO^\cdot)^{1/2}(M) \quad (46)$$

Again, assuming the steady state for (BzO^\cdot) , the following equation will be drawn:

$$\frac{d(BzO^\cdot)}{dt} = k_i(Bz_2O_2)(DMA) - k_t(BzO^\cdot)(M) = 0 \quad (47)$$

From the above-mentioned equation, the following expression is readily obtained:

$$R = \frac{k_p k_i^{1/2}}{k_t^{1/2}} (M)(Bz_2O_2)^{1/2}(DMA)^{1/2} \quad (48)$$

3. Suspension Polymerization of Styrene

The polymerization of styrene in solution [53,58] and bulk [54,55,59–61] by the redox system benzoyl peroxide–di-*n*-alkylaniline has been studied considerably by many researchers. Different dialkylanilines (DAAs) such as dimethylaniline (DMA), diethylaniline (DEA), di-*n*-butylanilines, di-*n*-octylaniline, and di-*n*-decylaniline combined with benzoyl peroxide have been studied for the solution polymerization of styrene [58] in benzene at 30°C. It was found that the initial rate of polymerization increased with a decrease of the molar ratio of Bz_2O_2 /DAA for a specific concentration of monomer and Bz_2O_2 . The degree of polymerization decreased with the decrease of molar ratio of Bz_2O_2 /DAA. The initiator efficiency seemed to increase gradually with the number of carbons of the alkyl groups in the DAAs, with the exception of di-*n*-octylaniline.

The kinetics of the bulk polymerization of styrene has been studied in detail at 30°C and 60°C by a dilatometer [60] using the benzoyl peroxide–dimethylaniline redox system. Also, the initiating efficiency of the ring-substituted diethylanilines–benzoyl peroxide system [61] at 30°C for styrene polymerization has been reported. A mathematical treatment for the free-radical production by Bz_2O_2 –DMA has been derived for the styrene polymerization [55,59] at 0°C. The initial rates of polymerization R_p^0 for 30°C and 60°C are as follows:

At 30°C,

$$R_p^0 = 1.67 \times 10^{-3} ([Bz_2O_2][DMA])^{0.497} \quad (49)$$

At 60°C,

$$R_p^0 = 5.25 \times 10^{-3} ([Bz_2O_2][DMA])^{0.418} \quad (50)$$

The results of O'Driscoll and Schmidt [60] were different from those of Meltzer and Tobolsky [54] for R_p^0 (initial rate of polymerization) as a function of the catalyst concentration. In the latter work, it was shown that the rate law $R_p^0 = K([Bz_2O_2][DMA])^a$ held over a wide range of catalyst concentrations and temperatures. The value of the exponent a was 0.5 at low temperatures, as expected for a bimolecular reaction between amine and peroxide. At 30°C, 45°C, and 60°C, the values found by Meltzer and Tobolsky [54] were 0.39, 0.38, and 0.33, respectively. However, according to O'Driscoll and Schmidt [60], these values were 0.5 and 0.42 at 30°C and 60°C, respectively. The lower value at 60°C may be attributed to the existence of an induction period at the lower catalyst concentration.

In conclusion, it was shown that the kinetics of polymerization are the same at higher and lower temperature. The efficiency of the reaction in initiating polymerization seems to fall slightly with increasing temperature.

4. Suspension Polymerization of Methyl Methacrylate

Lal and Green [56] have studied extensively the bulk polymerization of methyl methacrylate at 25°C using various amines, mostly tertiary amines. The total yield of polymer depends on the heat developed during polymerization as well as the production of free radicals. The rate of polymerization increased or decreased with the substitution at the para position of dimethylaniline by electron-donating groups or electron-withdrawing groups, respectively. Aliphatic tertiary amines are much less reactive than aromatic tertiary amines for accelerating polymerization, whereas primary amines, aliphatic as well as aromatic, act as inhibitors. Substitution of the methyl groups in dimethylaniline by ethyl groups does not change the reactivity of the amine for accelerating the polymerization; however, when propyl groups are substituted for methyl groups, the reactivity is somewhat reduced. Replacement of methyl groups in dimethylaniline by hydroxy ethyl groups does not materially affect the reactivity of the amine for accelerating polymerization. Tribenzylamine decomposes benzoyl peroxide very rapidly (less than 5 min), but no polymer is obtained in the bulk polymerization of methyl methacrylate. The amine may function as its own inhibitor. The molecular weights of the polymers obtained are in the neighborhood of $120,000 \pm 10,000$ in the case of trialkylamines.

Very recently, the feasibility of aliphatic tertiary amine like the triethylamine–benzoyl peroxide redox-initiating system in photopolymerization of methyl methacrylate [66] has been reported. In the dilatometric study of methyl methacrylate polymerization at 35°C with various solvents, the initiator exponent was 0.34. The monomer exponent depends on the solvents used. In acetonitrile, pyridine, and bromobenzene, the monomer exponent was 0.5, 0.67, and 1.1, respectively, within the concentration range studied. Benzene and chloroform give first-order dependence of rate on [monomer] and behave as normal (inert) diluents. The activation energy was 3.2 kcal mol⁻¹.

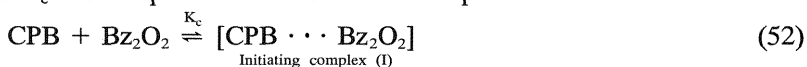
E. Quarternary Ammonium Salts as Reductants

Quarternary salts in combination with benzoyl peroxide are known to induce vinyl polymerization in emulsion systems [79,80]. Quarternary salts are also potential photoinitiators for vinyl polymerization [81]. The use of quarternary salts in combination with peroxides as redox initiators for suspension polymerization of styrene [82] and polymerization of methyl methacrylate [83,84] in bulk or in solution have been explored.

The polymerization of MMA with the cetyltrimethyl ammonium bromide (CTAB)–Bz₂O₂ redox system [84] and the cetylpyridinium bromide (CPB)–benzoyl peroxide redox system [83] was strongly inhibited by hydroquinone while the inhibitory effect of air or oxygen was marginal. A radical mechanism is thus indicated. End-group analysis for amino end groups by the dye technique [85] clearly indicated the incorporation of basic (amino) end groups. When a dilute solution of Bz₂O₂ was mixed with an equal volume of a dilute solution of quarternary salt, for example, CPB, the UV absorption spectrum of the mixture was not the average of the spectra of the two solutions. The absorbance difference may be attributed to the rapid equilibrium between the formation of a complex and the components. Thus, the species effective for initiating polymerization appears to be the complex of the peroxide and CPB which subsequently decomposes by a radical mechanism. The concentration of the initiating species [I] in the polymerization may be expressed as

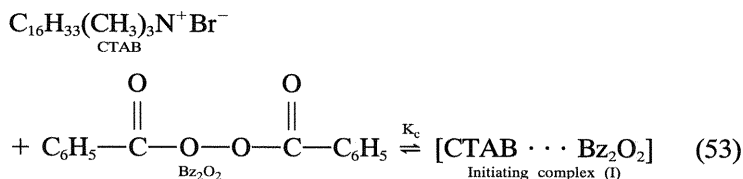
$$[I] = K_c[CPB][Bz_2O_2] \quad (51)$$

where K_c is the equilibrium constant for complexation:

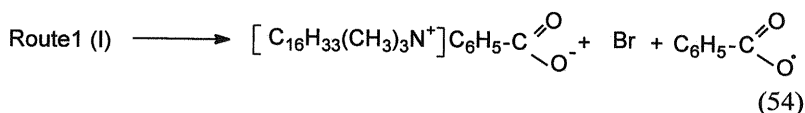


The mechanism is similar to that of the cetyltrimethyl ammonium bromide–benzoyl peroxide redox system. The radical generation process may be considered to include the following steps:

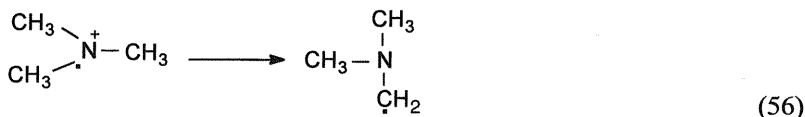
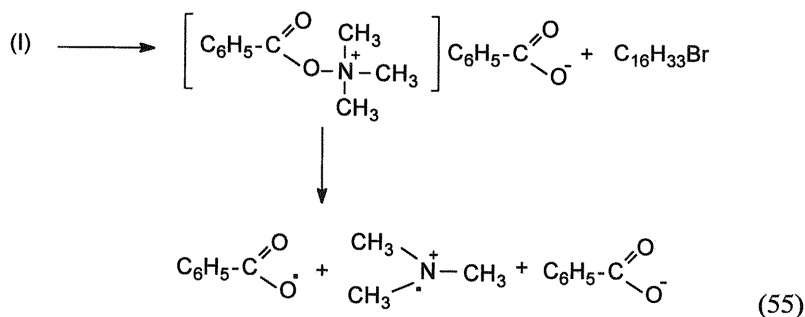
(a) Complexation



(b) Radical generation



Route 2



The radical generation step is apparently influenced by monomer (M) and solvent molecules (S) which possibly compete in reaction with the initiating complex (I). The radical generation reactions influenced by monomer and solvent may then be expressed as



The rate of initiation R_i may then be written as

$$R_i = K_c[\text{CATB}][\text{Bz}_2\text{O}_2] (k_1[\text{M}] + k_2[\text{S}]) \quad (59)$$

1. Suspension Polymerization of Methyl Methacrylate

The polymerization of methyl methacrylate was studied dilatometrically at 40°C under bulk and high-dilution conditions using CPB–Bz₂O₂ [83] and CTAB–Bz₂O₂ [84] redox system in polar solvents such as alcohol, acetone, or dimethyl formamide. The effect of several solvents/additives on the polymerization revealed that dimethyl formamide (DMF), acetonitrile, and pyridine acted as rate-enhancing solvents; benzene, methanol, chloroform, and acetone acted as inert diluents; formamide and acetamide cause pronounced retardation. In the case of the CTAB–Bz₂O₂ system under bulk condition (using DMF 10% of the total), the rate was practically independent of [Bz₂O₂] up to 0.025 M, whereas the kinetic order with respect to CTAB was about 0.16 for a concentration up to 0.001 M. At high dilution (DMF 50% of the total), the rate of polymerization was proportional to [Bz₂O₂]^{0.5} and [CTAB]^{0.5}. At the high-dilution condition in DMF (50% v/v), R_p increased with [Bz₂O₂] up to 0.025 M and remained constant with a further increase in [Bz₂O₂]. R_p increased with increasing [CTAB] up to 0.001 M and then decreased with a further increase in [CTAB]. It was found that R_p increased with increasing DMF content up to about 30%. This accelerating effect of DMF was not apparent with further dilution and the usual effect of monomer concentration was found, the order with respect to the monomer being unity. The overall activation energy was 11.2 kcal mol⁻¹.

However, in the case of the CPB–Bz₂O₂ initiating system, R_p was proportional to ([CPB][Bz₂O₂])^{0.18} both in near-bulk and high-dilution conditions. The [CPB] was between 0.1×10^{-3} and 8×10^{-3} M and [Bz₂O₂] was between 3×10^{-3} and 100×10^{-3} M. The activation energy for polymerization was 13.6 kcal mol⁻¹. DMF, acetonitrile, and pyridine acted as rate-enhancing solvents in the redox polymerization, whereas formamide and acetamide behaved as retarding additives.

2. Suspension Polymerization of Styrene

In the case of suspension polymerization of styrene [82] using the Bz₂O₂–lauryl puridinium chloride redox system, about 100% conversion with 1-mm-diameter polystyrene beads were obtained using the typical recipe presented in Table 7.

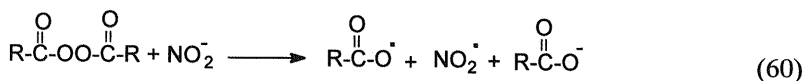
Table 7 Typical Recipe: Suspension Polymerization of Styrene^a

Ingredients	Amount (g)
Water	1000
Styrene	900
3 μ Mg silicate	0.5
Benzoyl peroxide	2.7
Lauryl pyridinium chloride	0.03
<i>tert</i> -Butyl perbenzoate	3.6

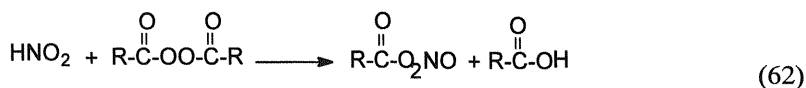
^aPolymerization for 10 hr at 80–120°C.

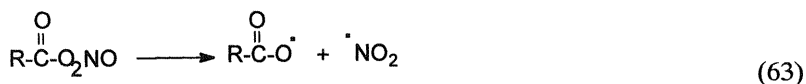
F. Nitrite as Reductant

The reaction between hydrogen peroxide and sodium nitrite was studied in detail by Halfpenny and Robinson [86] in 1952. The characteristics of the reaction, particularly in the presence of a bromide ion, and the evolution of oxygen with certain concentration of peroxides suggested the possible formation of free radicals. They demonstrated their occurrence by observing the polymerization of methyl methacrylate. In the early fifties, Schulz et al. [87] had reported the acrolein polymerization by H_2O_2 – NaNO_2 as a redox initiator. The reports of the use of nitrites as a reducing agent in polymerization are very few. Patent literature reports the suspension polymerization of vinyl pyridine [88] and vinyl chloride [89] using NaNO_2 as the reducing agent in combination with acyl peroxides like Bz_2O_2 or lauroyl peroxide. The mechanism may be written in one step as follows:

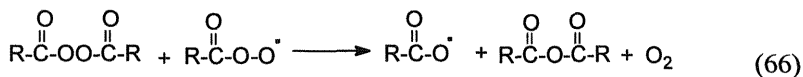
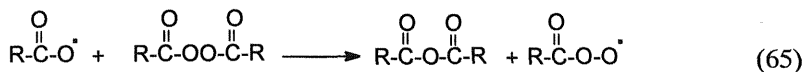


According to Halfpenny and Robinson [86] in the light of the mechanism for the H_2O_2 –nitrite redox system, the various steps of the reaction system may be written as follows:





When peroxide is abundant, the acyl radical provides a means of oxygen liberation according to the following reactions:



The above free radicals take part in the initiation and the termination processes in polymerization.

1. Suspension Polymerization of Vinyl Chloride

Vinyl chloride [89] with or without a comonomer has been suspension polymerized using a mixed-catalyst system (i.e., lauroyl peroxide and 2-ethylhexyl peroxydicarbonate) with a reducing agent NaNO_2 in two reactors maintained at different temperatures. The polymerization was carried out according to the typical recipe presented in Table 8. After 50 hr, the conversion values in the first and second reactors were 15% and 90%, respec-

Table 8 Typical Recipe: Suspension Polymerization of Vinyl Chloride^a

Ingredients	Amount (ppm)
Water	140
Vinyl chloride	100
2-Ethylhexyl peroxydicarbonate	0.04
Lauroyl peroxide	0.01
80% Saponified poly(vinyl acetate)	0.07
NaNO_2	0.002

^aPolymerizations at 61°C in the first reactor and at 57°C in the second reactor for 50 hr.

Table 9 Typical Recipe: Suspension Polymerization of Vinyl Pyridine^a

Ingredients	Amount (ppm)
Water	800
4-Vinyl pyridine	247
Styrene	62
Benzoyl peroxide	4
Dioctyl phthalates	50
NaCl	234
NaNO ₂	2.9
Hydroxyethyl cellulose	4.5

^aPolymerizations for 9 hr at 80°C at a stirring rate of 250 rpm.

tively, and no side-wall deposition was noted. The polymer had a weight-average degree of polymerization (DP) of 1020, a plasticizer absorbability of 29.2%, a thermal stability of 75 min, and a gel time of 2.5 min. The product prepared by polymerization at 58°C in both reactors had a weight-average DP of 1010, a plasticizer absorption of 24.8%, a thermal stability of 65 min, and a gel time of 4.0 min.

2. Suspension Polymerization of Vinyl Pyridine

Vinyl pyridine with or without comonomers was polymerized by suspension polymerization [88] in H₂O in the presence of fatty acid esters or phthalates to give polymers in spherical powder form. The polymerization was carried out according to the recipe provided in Table 9 to yield a final product of 850 ml of yellow transparent spherical copolymer beads. When dioctyl phthalate was omitted, a similar composition yielded large lumps.

III. ALKYL PEROXIDE

Alkyl peroxides are extensively used for the suspension polymerization of styrenic monomers [90–93] and vinyl chloride [94,95].

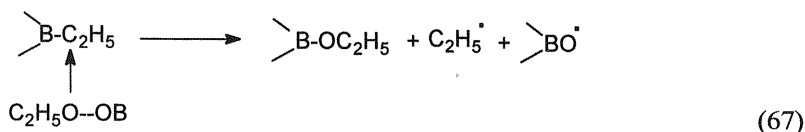
A. Alkyl Boron as Reductant

Alkyl boron compounds can initiate the polymerization of vinyl monomers in the presence of a suitable cocatalyst. A common feature of the cocatalyst

(i.e., peroxides [96–98], hydroperoxides [99], amines [100], and organic halides [101]) is that it can be considered as an “electron-donating” compound. In most of the systems investigated, it has been established that the reaction is a free-radical polymerization [101–104], but the rate equation is not simple, suggesting a complex mechanism in which coordination of the organometallic compound is a rate-determining step [100,101,105]. Furthermore, the reaction order changes when the organometallic compound to cocatalyst ratio changes for peroxides [97], oxygen [102–104,106,107], hydroperoxides [99], hydrogen peroxide [108], and organic halides [101]. This change of order, which may be a consequence of complex formation is attributed to various causes [101,106,108], but in most cases, no satisfactory explanation is given.

The oxidation of trialkylborons by molecular oxygen generally produces alkoxy boron compounds via intermediate peroxides [109,110], although Mirviss [111] has reported hydrocarbons among the products. In addition, vinyl monomers polymerize at room temperature in the presence of trialkylborons and air [112]. Free radicals are evidently produced at some stage in the reaction. Free radicals have been assumed to arise from the homolytic decomposition of peroxidic intermediates [111,113] even though these peroxides are very stable at room temperature [110]. Others have suggested that the free radicals are produced in a reaction between the peroxide and unoxidized trialkylboron [98,114].

The high rate of peroxide formation in the oxidation of triethylboron seems to rule out the possibility of a long-lived oxygen–triethylboron complex which rearranges to the peroxide. This has been stated by various authors [109–111]. Only Zutty and Welch [109] have provided experimental evidence in the case of tri-*n*-butylboron. A transient intermediate cannot be excluded. There is no indication that free radicals arise during the oxidation of triethylboron. Both triethylboron and peroxide were required to initiate vinyl polymerization of methyl methacrylate in agreement with Bawn and co-workers [98]. The results [104] indicate that the ethyl radical was produced in a reaction between triethylboron and the peroxide, wherein the peroxide was reduced. There was no evidence for the presence of the ethoxy radical arising from homolytic decomposition of the peroxide. Iodine was an efficient trap for the ethyl radical. From the work of Hansen and Hamman [104], it is indicated with some uncertainty that the reduction is a 1:1 reaction. It is unlikely that the ethyl radical was the only one produced, but the structure of a companion radical could not be ascertained. The amount of iodine consumed indicates that radicals were not produced in each reactive act. A possible explanation [115] is that the reduction is a “cage reaction”:



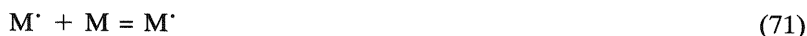
The formation of a cage should be especially favored by coordination of one of the oxygen atoms to boron. Radical recombination would lead to the alkoxy compounds commonly observed, whereas diffusion from the cage could lead to the products derived from free radicals.

Recently, Abuin et al. [96] investigated the kinetic features of bulk polymerization of methyl methacrylate using triethyl boron (TEB)–di-*tert*-butylperoxide mixture as the radical initiator. From their data, it can be seen that, working at a constant di-*tert*-butylperoxide concentration, the reaction rate increases as the TEB concentration increases, reaching a maximum and then decreasing with further TEB addition. If the TEB only modifies the initiation rate, a simple free-radical mechanism would predict that at a given temperature, the following equation should hold true:

$$R\lambda = \text{constant} \quad (68)$$

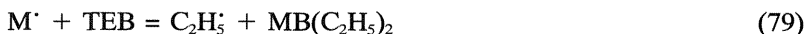
where R is the measured polymerization rate and λ is the mean chain length.

However, their data show that, at a high TEB concentration, the product ($R\lambda$) decreases when TEB increases. This effect can be related to the occurrence of chain transfer to the organometallic compound. The data can be treated according to the following reaction scheme:



where M , X , and R^\cdot represent monomer, peroxide, and radical, respectively.

The chain transfer reactions are considered to be



A reaction similar to reaction (79) has been reported as being extremely fast for several radicals conjugated to a carbonyl group [116].

Initiation by TEB–di-*tert*-butyl peroxide (DTP) shows [97] the following main characteristics: (i) At low (TEB/DTP), the initiation step follows a rate law represented by

$$R_i = k_{80}(\text{TEB})(\text{DTP}) \quad (80)$$

(ii) When the peroxide concentration is kept constant, the rate of initiation increases, reaching a maximum and then decreasing when the TEB concentration increases.

The following mechanism is consistent with these findings:



where C_1 and C_2 represent complexed forms of the TEB. The proposed mechanism gives the following expression for the rate of initiation:

$$R_i = \frac{k_{83}K_{81}(\text{MMA})(\text{DTP})_0(\text{TEB})}{1 + K_{82}(\text{TEB})^2} \quad (84)$$

where $(\text{DTP})_0$ is the total peroxide concentration, (TEB) is the concentration of TEB uncomplexed, and K_{81} and K_{82} are the equilibrium constants of reactions (81) and (82), respectively. The concentration of uncomplexed TEB can be obtained from the total concentration $(\text{TEB})_0$ by solving

$$(\text{TEB})_0 = \frac{(\text{TEB})[1 + K_{81}(\text{MMA})] + 2K_{82}(\text{DTP})_0(\text{TEB})^2}{1 + K_{82}(\text{TEB})^2} \quad (85)$$

Similarly, for a rate at low $(\text{TEB})_0$, Eq. (84) reduces to

$$R_i = \frac{k_{83}K_{81}(\text{MMA})(\text{DTP})_0(\text{TEB})_0}{1 + K_{81}(\text{MMA})} \quad (86)$$

Similarly, the maximum rate for a given $(\text{TEB})_0$ could be derived to be

$$(R_i)_{\max} = \frac{k_{83}K_{81}(\text{MMA})(\text{DTP})_0}{2K_{82}^{1/2}} \quad (87)$$

Table 10 Bulk Polymerization of Methyl Methacrylate at 50°C

[t-Butyl peroxide] (mol L ⁻¹)	[TEB] (mol L ⁻¹)	Time (min)	Conversion % (% L ⁻¹)	E (kcal mol ⁻¹)
0.062	0.034	60	3.2	10.0
		60	4.1	
		135	9.7	
0.062	0.063	60	6.0	
		60	5.5	
		100	10.3	
		120	10.9	

Bulk Polymerization of Methyl Methacrylate

Methyl methacrylate [97] was bulk polymerized at 50°C using t-butyl peroxide–triethylboron(TEB) as the initiator. The rate of initiation by the mixture of triethylboron and t-butyl peroxide was first order with respect to peroxide. The order in triethylboron changes from 1 at a low triethylboron/peroxide ratio to nearly zero at a high triethylboron/peroxide ratio. The results [97] are given in Table 10.

Abuin et al. [96] also reported the bulk polymerization of methyl methacrylate at 20°C using triethylboron–di-t-butylperoxide at various triethylboron concentration. The amount of polymer produced was proportional to the reaction time. The results are presented in Table 11.

Abuin et al. [96] have also compared the rate of polymerization initiated by the mixture containing different peroxides and it is found that the rate with dimethyl peroxide is nearly 32 times faster than with di-*tert*-bu-

Table 11 Bulk Polymerization of Methyl Methacrylate at 20°C

[TEB] (10 ⁻² M)	[DTP] ^a (M)	Rate of polymerization ^b (×10 ⁻⁶ m sec ⁻¹)	Mean chain length
1.18	0.062	3.65	5000
6.80	0.062	4.50	4000
15.40	0.062	4.14	3800
24.50	0.062	2.74	5500
38.80	0.062	2.50	5000

^aDTP = Di-t-butyl peroxide.

^bAveraged over 185 min reaction time.

tylperoxide as a cocatalyst. This difference can be attributed to the steric hindrance introduced by the bulky *tert*-butyl groups. Similarly, it is interesting to note the difference between TEB and triethyl aluminum (TEA) as the cocatalyst with peroxides. With TEB, alkyl and acyclic peroxides show similar cocatalytic activities [97]. On the other hand, it has been reported that TEA is only active when acyl peroxides are employed [117]. This difference can be related to the monomeric state of TEB; TEA is mainly present as a dimer [117].

IV. PERESTERS (PEROXYESTERS OF CARBONIC ACID)

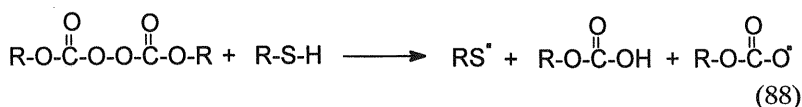
Although peroxydicarbonates are useful low-temperature initiators for vinyl polymerization [118,119], little has been published about the characteristics of their thermal decomposition. The rate of decomposition was determined for several of these compounds ($[\text{ROC}(\text{O})\text{O}]_2$, $\text{R} = \text{Et}$, $i\text{-Pr}$, PhCH_2 , $\text{NO}_2\text{CMe}_2\text{CH}_2$ [120]; $\text{R} = i\text{-Pr}$ [104]) in the early 1950s. Razuvaev et al. have since added others to the list ($\text{R} = \text{Me}$, Bu , $i\text{-Bu}$, $t\text{-Bu}$, *amyl*, *cyclohexyl* [122], and *Ph* [123, 124]). There is a belief that peroxydicarbonates are particularly sensitive to radical-induced decomposition [119–121]. This is undoubtedly true for the pure substances [119,120]. The addition of 1% of iodine to pure diisopropyl peroxydicarbonate reduces [120] the rate of decomposition by a factor of 60. Among all the percarbonates, phenyl peroxydicarbonate [123,124] may prove to act differently because decarboxylation yields the resonance-stabilized phenoxy radical. This peroxide is said to be more labile than other peroxydicarbonates and inhibits [123] rather than initiates polymerization [124]. Peroxydicarbonates are very efficient initiators for the suspension polymerization of vinyl chloride [125–139], vinylidene fluoride [16], and styrene [17], and the copolymerization of vinyl acetate [18,19] with other monomers. Peroxydicarbonates [140–143] are also proved to be efficient-radical initiators in conjunction with various reducing agents for vinyl polymerization.

A. Mercaptans as Reductant

Mercaptans have been proved to be an efficient reducing agent with H_2O_2 [144,145] to initiate vinyl polymerization. It has also been used with Bz_2O_2 [146] for emulsion polymerization of vinyl monomers. The activation of persulfate by reducing agent such as thiols [147–155] has been extensively studied and the combination has been used for vinyl polymerization. Stark-

weather et al. [156] and Kolthoff et al. [157,158] have demonstrated the catalytic effect of thiols in persulfate-initiated emulsion polymerization of styrene with or without butadiene.

The use of 2-mercaptoethanol as reducing agent in conjunction with peroxydicarbonate for the suspension polymerization of vinyl chloride [159,160] has been reported in the patent literature. During the redox reaction, hydrogen is extracted from thiol by the homolysis of the $-S-H$ group to give a sulfur radical. The mechanism may be proposed as follows:



Suspension Polymerization of Vinyl Chloride

Suspension polymerization of vinyl chloride has been reported using 2-mercaptoethanol as a reductant with bis (2-ethylhexyl) peroxydicarbonate [160] and diisopropyl peroxydicarbonate [159]. Thus, in the case of (2-ethylhexyl) peroxydicarbonate [160], mixtures of vinyl chloride with or without comonomers 100, C_{2-6} compounds, having $-SH$ and $-OH$ groups 0.001–0.1 ppm, C_{4-18} alkyl vinyl ether 0.01–1.0 ppm, and benzyl alcohol with or without C_{1-4} alkyl substituents 0.01–1.0 ppm are stirred to give PVC or copolymers having equally good porosity, heat stability, and processability.

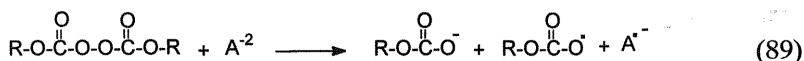
In the case of diisopropyl peroxydicarbonate [159], an 80–20:20–80 mixture of partially saponified poly(vinyl acetate) and a cellulose ether was used as the dispersing agent. The suspension polymerization or copolymerization of vinyl chloride was carried out in the presence of a compound having a $-SH$, $-OH$, or $-CO_2H$ groups in order to reduce the amount of chain transfer agent required.

B. Sulfide and Dithionate as Reductant

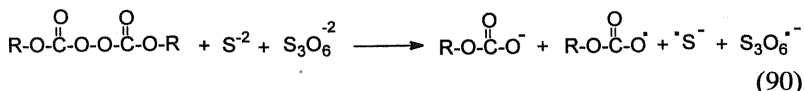
The oxyacids of sulfur such as sulphite, bisulfite, bisulfate, thiosulfate, metabisulfite, and dithionate proved to be efficient reducing agents in the redox-initiated polymerization of vinyl monomers. Numerous articles in these areas have been reported in the literature. Palit et al. [161–164] and Roskin et al. [165–167] have reported the polymerization of vinyl monomers using the persulfate–dithionate redox system. Chaddha et al. [168] also reported the persulfate–sulfide redox system to initiate polymerization. The use of sulfide [169,170] and dithionate [171] as reducing agents in conjunction with organic hydroperoxide, like cumene hydroperoxide and iron salt in emulsion

polymerization, has been described. Tadasa and Kakitani have reported the suspension polymerization of vinyl chloride by percarbonate–sodium sulfide [172] and percarbonate–sodium dithionate [173] systems.

The general initiation reaction in these systems can be schematically represented as



where A is sulfide or dithionate;



These indicated radicals initiate polymerization.

Suspension Polymerization of Vinyl Chloride

The presence of sulfide or dithionate also prevents scale formation during polymerization. Thus, in the system dioctyl peroxydicarbonate–sodium sulfide [172], vinyl chloride with or without vinyl comonomers was polymerized in the presence of 0.1–1000 ppm (based on monomers) inorganic sulfides according to the recipe presented in Table 12 to give PVC with good heat stability, with no scale formation, compared with 450 g m⁻² for a similar run without Na₂S_x.

Similarly, in the case of dioctyl peroxydicarbonate–Na₂S₃O₆ [173], the polymerization was carried out according to the recipe in Table 13 to give PVC with good heat stability. Scale formation in the above polymerization was 5 g m⁻², compared with 550 g m⁻² for a similar run without Na₂S₃O₆.

Table 12 Typical Recipe: Suspension Polymerization of Vinyl Chloride by Dioctyl Peroxydicarbonate–Sodium Sulfide System^a

Ingredients	Amount (ppm)
Water	150
Vinyl chloride	100
Partially saponified poly(vinyl acetate)	0.1
Dioctyl peroxydicarbonate	0.05
Na ₂ S _x	0.01

^aPolymerization under stirring for 5.8 hr at 58°C.

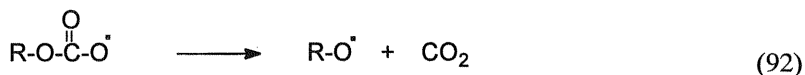
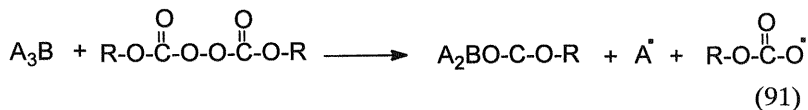
Table 13 Typical Recipe: Suspension Polymerization of Vinyl Chloride by Dioctyl Peroxydicarbonate– $\text{Na}_2\text{S}_3\text{O}_6$ System^a

Ingredients	Amount (ppm)
Water	150
Vinyl chloride	100
Partially saponified poly(vinyl acetate)	0.1
Dioctyl peroxydicarbonate	0.04
$\text{Na}_2\text{S}_3\text{O}_6$	0.001

^aPolymerization under stirring for 6.4 hr at 58°C.

C. Alkyl Borane as Reductant

In spite of the great number of investigations [106,112,114,174–177] in which alkyl boron compounds were used as initiators of vinyl polymerization, most of the main features of the mechanism involved for the initiating system, such as alkyl boron compounds in the absence of air [106,113,114, 175,178–181], peroxides or hydroperoxides in conjunction with trialkylboron (A_3B) compounds [98,99,182] have not yet been demonstrated. The reports on a percarbonate–alkyl boron redox system for vinyl polymerization are very few. The bulk polymerization of vinyl chloride by the redox system consisting of diisopropyl peroxydicarbonate–triethylboron has been reported by Ryuichi and Isao [183]. Ryabov et al. [184] also reported the low-temperature polymerization of vinyl chloride by the dicyclohexyl peroxydicarbonate–tri-*n*-butylboron redox system. In the light of mechanism described by Contreras et al. [97], the following mechanism may be suggested for the percarbonate–alkyl boron system:



Bulk Polymerization of Vinyl Chloride

In the case of the diisopropyl peroxydicarbonate–triethylboron redox system [183], 26.4% di-butyl phthalate solution containing 0.01624 g of diisopropyl peroxydicarbonate was chilled to -78°C in a pressure vessel, 15 g of vinyl chloride was added followed by 6.928×10^{-5} mol Et_3B in hexane under

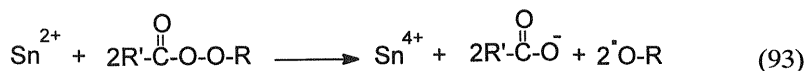
nitrogen, and the mass was kept at -20°C for 7 hr to give 4.4% polymerization. Similar polymerization at 10°C with 0.02706 g of Et_3B produced 16.64% polymer, but no polymer was obtained with the use of diisopropyl peroxydicarbonate alone.

V. PERESTERS (PEROXYESTERS OF CARBOXYLIC ACID)

Peroxyesters of carboxylic acids have been extensively used for the suspension polymerization of vinyl monomers (Table 14). Several patents have appeared on the suspension polymerization of vinyl chloride [185–188], styrenic monomers [189,190], and methyl methacrylate [191].

A. Sn^{2+} Salts as Reductant

The decomposition of a peroxyester by a stannous salt involves 2 mol of perester since the oxidation of stannous ion to stannic is a two-electron transfer, that is,



The stoichiometry shown indicates that a 2:1 perester/ Sn^{2+} mole ratio should result in complete perester decomposition. However, this is not in accord with the experimental observation in the reaction [192,193] between *t*-butyl peroctoate (TBPO) and stannous octoate (SnOct); that is, the decomposition occurs rapidly to the extent of approximately 40% and then the TBPO concentration remains unchanged. This may be attributed to the requirement for the availability of stannous ion and the failure of stannous

Table 14 Peroxyesters for Vinyl Monomers Polymerization

Initiators	Monomers
<i>tert</i> -Bu peroxyneodecanoate	Vinyl chloride
2,4,4-Trimethylpentyl peroxyphenoxyacetate	Vinyl chloride
Diphenyl peroxyoxalate	Vinyl chloride
Di- <i>tert</i> -Bu diperoxyazelaate	Styrene
Di- <i>tert</i> -Bu peroxyhexahydroterephthalate	α -Methyl styrene/styrene/acrylonitrile
<i>tert</i> -Bu 2-ethylhexane peroxyoate	Styrene
<i>tert</i> -Bu peroxy-2-ethylhexanoate	Methyl methacrylate

octoate to undergo ionic dissociation; that is, stannous octoate may possess some covalent character.

It is noteworthy that the analytical procedure for the quantitative determination of TBPO involves reaction with excess stannous chloride in an aqueous medium, followed by back titration of excess stannous ions. The aqueous medium results in the hydrolysis of stannous chloride to produce a solution of stannous hydroxide in aqueous hydrochloric acid. Stannous octoate may not hydrolyze in a neutral aqueous medium. Thus, the absence of complete dissociation and/or hydrolysis prevents the stoichiometric interaction of stannous octoate and TBPO. The possible presence of a TBPO–stannous octoate complex may also play a role in the failure to complete the reaction, as suggested by the observed presence of residual peroxide and residual stannous ions after the decomposition of TBPO has proceeded to the maximum extent.

The presence of a vinyl chloride monomer (VCM) has been shown to reduce even the limited extent of BPO decomposition by stannous octoate. This may be attributed to a VCM–stannous octoate complex, whose presence has been experimentally confirmed [192]. Apparently, the stannous octoate in this complex, which contains VCM and stannous octoate in a 1:2 molar ratio, dissociates or hydrolyzes or interacts in some other manner with TBPO (e.g., by complexation with the carbonyl group) to an even lesser extent than stannous octoate in the absence of VCM.

It would appear that the failure to achieve the theoretical complete decomposition of TBPO at a 2:1 TBPO/ Sn^{2+} ratio is due to the unavailability of Sn^{2+} in the concentration necessary to achieve the indicated stoichiometry. Thus, the TBPO–stannous octoate complex and the VCM–stannous octoate complex reduce the availability of stannous octoate for TBPO decomposition. Further, if the decomposition of TBPO requires the presence of a stannous ion, the incomplete hydrolysis or dissociation of stannous octoate per se or completed with TBPO and/or VCM, under the decomposition condition, reduces the availability of a stannous ion.

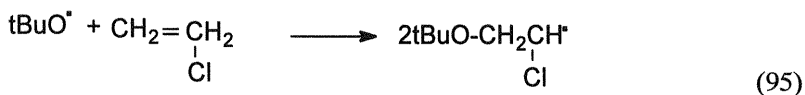
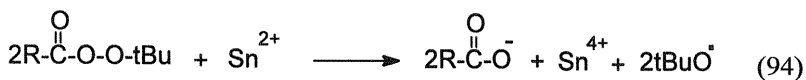
It is obvious that a route to effective, stoichiometric decomposition of TBPO in the presence of a stannous salt requires complete dissociation or hydrolysis of the latter through a change in reaction condition (e.g., an acidic pH) or the use of a more rapidly hydrolyzed stannous salt. It should be noted that stannous chloride, which generates an acidic medium on hydrolysis, quantitatively decomposes TBPO. Further, stannous laurate, which contains the lauroate moiety, in the presence of emulsifiers such as sodium lauryl sulfate or dodecylbenzene sulfonate results in a more rapid polymerization rate and a higher conversion of VCM than stannous octoate, indicative of a greater availability of the effective reductant (i.e., a stannous ion). The stannous laurate may be solubilized in the aqueous phase and the resultant mi-

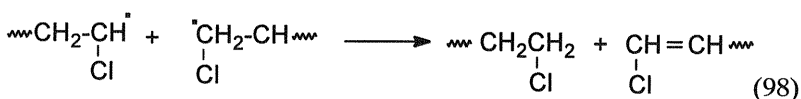
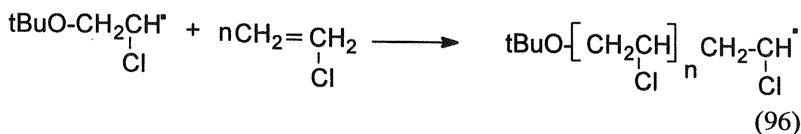
croenvironment promotes hydrolysis and/or dissociation, in contrast to the situation with water-insoluble stannous octoate and stearate.

Because it is necessary to increase the availability of the stannous salt for hydrolysis and/or dissociation, it is desirable to utilize an additive which competes with TBPO and VCM in complex formation with stannous salts. In this connection, it has been noted that the decomposition of TBPO in the presence of stannous octoate proceeds to a greater extent when an ester such as ethyl acetate is present. Further, the suspension system contains esters such as sorbate esters and an ethereal compound (i.e., methylcellulose) and promotes a more complete decomposition of TBPO and polymerization of VCM. Both ester groups and ethereal oxygen have the ability to complex with metal compounds, including stannic and stannous derivatives, and can therefore effectively compete with TBPO and/or VCM in complex formation.

An important point to be considered is the necessity to generate radicals from TBPO on a continuous basis in order to achieve effective polymerization. If the hydrolysis and/or dissociation of a stannous salt occurs rapidly and promotes rapid TBPO decomposition, the resultant radicals may be generated too rapidly for effective initiation of VCM polymerization to high conversions to high-molecular-weight PVC. Thus, it is necessary to promote the formation or release of reactive reductant at the desired rate throughout the polymerization period. It is also necessary to provide for complete decomposition of TBPO to yield PVC which does not contain residual TBPO.

The mechanism for the polymerization of VCM in the presence of TBPO–stannous octoate may be described as follows. The *t*-butoxy radical adds to VCM and initiates polymerization, in lieu of hydrogen abstraction. The reaction between the substrate radical (i.e., a VCM radical or the propagating chain radical) and the stannic ion results in the termination of the radical chain reaction and regeneration of the stannous ion. Thus, the latter is available for decomposition of BPO to generate additional chain-initiating *t*-butoxy radicals. However, the termination of chain growth results in an inefficient consumption of radicals:





Suspension Polymerization of Vinyl Chloride

Gaylord et al. have reported the suspension polymerization of vinyl chloride using the redox system, such as t-butyl peroxyoctoate– SnCl_2 [23,194] and t-butyl peroxyoctoate–stannous carboxylate [192,193]. The polymerization of VCM in the presence of the redox system has several unusual characteristics which can be explained on the basis of the description already made above.

1. The redox polymerization of VCM requires considerably higher TBPO concentration than the conventional thermal polymerization. The decomposition of TBPO at 50°C requires the presence of stannous octoate (SnOct) in some specific and reactive form, presumably stannous ions. In view of the unavailability of stannous octoate in this form, due to its complexation with TBPO and VCM as well as its failure to hydrolyze and/or dissociate, the concentration of active reductant is much lower than the amount of stannous octoate charged. Because the TBPO/ SnOct ratio is maintained constant, it is necessary to increase the amount of TBPO so that a sufficient amount of active reductant is available. It is also possible that the stannic species generated by the BPO oxidation of stannous octoate participate in the termination of propagating chains or interact with radicals generated from TBPO. It is well known that metals in the higher valance state (e.g., ferric and stannic compounds) react with free radicals and, as a result of electron transfer, convert the latter to cationic species which cannot add monomers such as VCM. It is, therefore, necessary to increase the TBPO concentration in order to provide additional radicals and the propagating chains therefrom, to compensate for those lost by electron transfer. The

coordination or complexation of stannous octoate with the chlorine atoms appended to the PVC chains may also reduce the concentration of stannous octoate available for TBPO reduction, as the PVC particles are insoluble in VCM and therefore remove the appended stannous octoate from the active locus of polymerization.

2. The redox polymerization generally does not go to completion except after extremely long reaction times and even then, the reaction mixture contains a large amount of undecomposed TBPO. Based on the decomposition studies, it also contains residual stannous species. The presence of undecomposed TBPO and stannous species at the leveling off or termination of VCM polymerization is consistent with the presence of TBPO-SnOct complex and/or the unavailability of reactive stannous species to complete the stoichiometric decomposition. Unhydrolyzed or PVC-bonded stannous octoate may be in the system, but not capable of reducing TBPO.

3. Although decomposition studies show that the decomposition of TBPO in the presence of stannous octoate proceeds rapidly to about 40% during the first 2 hr and then remains essentially unchanged over the next 20 hr, the polymerization continues for more than 10 hr. The indicated rapid decomposition of TBPO in the presence of stannous octoate does not occur when VCM is present. In fact, the decomposition rate is greatly reduced. This is actually desirable because the rapid decomposition generates radicals at a faster rate than VCM can add to it. Further, the presence of the suspending agents results in interference with the VCM-stannous octoate complex, possibly by forming a suspending agent-stannous octoate complex which slowly makes active stannous reductant available and therefore extends the time for radical generation, analogous to the behavior of peresters in thermal decomposition.

The suspension polymerization of VCM [23,194] in a bottle was carried out with the suspension recipe given in Table 15. The attempted polymerization of VCM in the presence of 0.055 ml (0.23 mmol) TBPO (0.5% by weight of VCM), in the absence of stannous chloride dihydrate, failed to yield any polymer after 20 hr at 50°C. This is consistent with the TBPO half-life of 133 hr at 50°C (10 hr half-life 74°C). The suspension polymerization of VCM in the presence of 0.5 wt% peroxyoctoate (POT), stannous chloride dihydrate 0.052 g (TBPO/SnCl₂ molar ratio = 1) and glacial acetic acid 2 ml resulted in a 5% yield of polymer after 13 hr at 50°C. The low yield of PVC indicated that the TBPO-SnCl₂ interaction either yielded predominantly nonradical products or proceeded so rapidly in the VCM droplet as to preclude effective polymerization. When the suspension polymerization of VCM in the presence of 0.5 wt% TBPO and VCM-insoluble stannous chloride dihydrate (POT/SnCl₂ molar ratio = 1) was conducted in the absence of acetic acid, the yield of PVC was 82% after 13 hr at 50°C. This

Table 15 Typical Recipe: Suspension Polymerization of Vinyl Chloride^a

Ingredients	Amount (ml)
Water	21
Polyoxyethylene sorbitan monostearate (1% aqueous solution)	1
Sorbitan monostearate (1% aqueous solution)	2
Methocel A15 (15 cps viscosity grade methylcellulose) (1% aqueous solution)	2
Vinyl chloride	10 g
TBPO	0.055

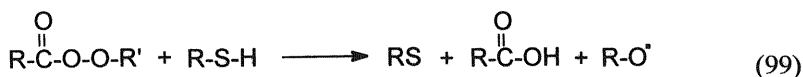
^aPolymerization for 20 hr at 50°C.

may be attributed to the interaction of the monomer-insoluble SnCl_2 or the hydrated ions thereof with the TBPO in the VCM at the water–monomer droplet interface to generate radicals at a slow useful rate.

In case of perester–stannous carboxylate redox system [192,193] with or without a complexing agent for vinyl chloride polymerization, the polymerization recipe was the same as described earlier for the SnCl_2 as reductant. In each case, 10 g of VCM was taken in the experiment for polymerization at 50°C. The conversion was increased in the presence of complexing agents. Some of the results are presented in Table 16.

B. Mercaptans as Reductant

The use of mercaptans as the reducing agent in the emulsion or aqueous polymerization of vinyl polymerization is not new. Its efficiency as the reducing agent in conjunction with oxidants like H_2O_2 [144,145], Bz_2O_2 [146], and $\text{K}_2\text{S}_2\text{O}_8$ [147–158] for vinyl polymerization has been reported. The feasibility of mercaptans [195–197] as the reductant with peroxyesters of carboxylic acid has been described for suspension copolymerization or graft copolymerization. The general mechanism may be written as



The above radicals take part in the initiation of polymerization.

Table 16 Vinyl Chloride Polymerization at 50°C with Perester–Stannous Carboxylate Redox System with or Without Complexing Agent

Stannous carboxylate (mmol)	TBPO ^a (mmol)	Complexing agent ^b type (mmol)	Time (hr)	Conv. %
Octoate 0.23	0.46	—	9	60
Octoate 0.23	0.46	—	11	80
Octoate 0.23	0.46	—	20	92
— —	0.46	—	20	0
Octoate 0.115	0.23	—	12	45
Stearate 0.115	0.23	—	18	30
Laurate 0.23	0.46	—	2	10
Laurate 0.23	0.46	—	6	40
Laurate 0.23	0.46	—	8	65
Laurate 0.23	0.46	—	10	90
Laurate 0.23	0.46	—	15	96
Laurate 0.115	0.23	—	9	45
Laurate 0.115	0.23	—	16	51
Laurate 0.115	0.23	DOP (0.23)	9	68
Laurate 0.115	0.23	DOP (0.23)	16	73
Laurate 0.046	0.092	—	7	15
Laurate 0.046	0.092	DOP (0.092)	7	23
Laurate 0.115	0.23	—	9	60 ^c
Laurate 0.115	0.23	DOP (0.23)	9	83 ^c
Laurate 0.115	0.23	DOA (0.23)	9	65
Laurate 0.115	0.23	2-EHA (0.23)	9	64
Laurate 0.115	0.23	TEP (0.23)	9	65

^aTBPO = t-butyl peroxyoctoate.^bDOP = dioctyl phthalate; EHA = ethylhexanoic acid; TEP = triethylphosphate.^cPolymerization at 55°C.

1. Suspension Graft Copolymerization of Styrene and Acrylonitrile to Polybutadiene Latex

In the suspension graft copolymerization [195], ABS polymers having enhanced physical properties like high impact strength and low polybutadiene content are prepared by graft copolymerization of styrene and acrylonitrile onto a polybutadiene polymer latex (particle size 1000–3000 Å, gel content 20–85%, and swell index ≈ 18 –150) in an aqueous medium in the presence of a suspending agent and a catalyst. The suspension graft copolymerization was carried out according to the typical recipe presented in Table 17 to yield ABS resin beads. The dried beads were blended with antioxidant and extruded to form pellets, which were molded to form a sample having Izod

Table 17 Typical Recipe: Suspension Graft Polymerization of Styrene and Acrylonitrile to Poly(butadiene) Latex^a

Ingredients	Amount (g)
Part A	
Styrene	521
Acrylonitrile	211
Antioxidant (as a 10% solution in acrylonitrile)	3.5
<i>tert</i> -Butyl peroxyphthalate	1.8
<i>tert</i> -Butyl peroxoate	0.54
<i>tert</i> -Dodecyl mercaptan	2.4
Part B	
Water	3050
Pliolite	2104
Latex	281
2.5% Solution of poly(vinyl alcohol)	700
0.5% Solution of poly(ethylene oxide)	100

^aPart A was added to Part B and the mixture was maintained at 68°C for 4 hr and at 100°C for 1 hr.

impact strength >13 ft-lb/in., tensile stress at yield 4500, elastic modulus 2.25×10^5 , and shear-Izod ratio <4.2.

2. Suspension Copolymerization of Acrylonitrile and Styrene

The acrylonitrile-styrene copolymer [196] was prepared by suspension polymerization in the presence of 0.005–0.5% (based on monomers) *tert*-Bu, 3,5,5-trimethyl perhexanoate, and *tert*-butyl peracetate at 110–140°C according to a typical recipe presented in Table 18 to give a copolymer (unreacted monomer 0.1%) with lower yellow neon and haze than a control (unreacted monomer) prepared without *tert*-Bu peracetate.

C. Alkyl Borane as Reductant

Alkyl borane as the reductant in redox polymerization is well known. It has been used previously in conjunction with alkyl peroxide and peroxyester of carbonic acid. The mechanism of alkyl borane-peroxyester of carboxylic acid is similar to that previously described. Suspension polymerization or copolymerization of vinyl chloride by the redox system such as monotertiary butyl permaleate–Et₃B or Bu₃B or iso-Bu₃B has been reported in patent literature [198].

Table 18 Typical Recipe: Suspension Copolymerization of Styrene and Acrylonitrile^a

Ingredients	Amount (g)
Water	25,000
Ca ₃ (PO ₄) ₂	150
Styrene	11,000
Acrylonitrile	6,000
<i>tert</i> -Butyl 3,5,5-trimethyl perhexanoate	25
<i>tert</i> -Butyl peracetate	15
<i>tert</i> -C ₁₂ H ₂₅ SH	50
Styrene	1,600

^aPolymerization for 5 hr at 100°C and 2 hr at 125°C.

Suspension Polymerization of Vinyl Chloride or Its Mixture

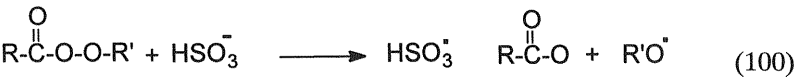
Vinyl chloride by itself or mixed with C₂H₄, propylene, or isobutylene is polymerized [198] in the presence of Et₃B, Bu₃B or iso-Bu₃B, and mono-*tert*-Bu permaleate at −30°C to +80°C. Thus, 500 g of vinyl chloride was polymerized at 20°C for 10 hr with 1200 cm³ of double-distilled H₂O, and 1.5 g of H₂O-soluble suspension stabilizer was introduced. Bu₃B (3.14 g) was introduced with the exclusion of oxygen and 4.0 g of mono-*tert*-Bu permaleate was added; 75.6% polymer conversion was achieved. Much lower yields of polymer were obtained when a peracetate or perbenzoate was used instead of the permaleate.

D. Bisulfite as Reductant

Bisulfite is one of the oldest reducing agents used in polymerization. Vinyl polymerizations using bisulfite as the reductant in conjunction with K₂S₂O₈ as the oxidant have been reported [155,199–215] as early as 1946. The use of bisulfite with H₂O₂ [199,216,217] as well as with organic peroxide like Bz₂O₂ [218] to initiate polymerization is also well known. The persulfate–bisulfite system has been used for the polymerization of acrylonitrile [204,219–222], methyl acrylate [223], styrene [211], chlorotrifluoro ethylene [201], and so forth. The bisulfite–persulfate combination along with Fe²⁺ has been also used to polymerize acrylonitrile [207,224]. Bisulfite is also used with other oxidants like peroxydicarbonate [225], Cr₂O₃ [226], oxygen [227], and KBrO₃ [227] for redox initiation. These initiating systems are only restricted to emulsion or aqueous polymerization. There are very few reports on suspension polymerization of vinyl chloride [228] and sus-

pension graft polymerization of vinyl pyridine to polyolefins [229] using a perester of the carboxylic acid–NaHSO₃ redox system.

In the light of the mechanism of persulfate–bisulfite redox initiation, the mechanism for the perester–bisulfite redox system may be suggested as follows:



The above radicals take part in the initiation process.

1. Suspension Polymerization and Copolymerization of Vinyl Chloride

Vinyl chloride [228] was polymerized and copolymerized in suspension at low temperature in the presence of a peroxide, a reducing agent, and a copper accelerator. Thus, the vinyl chloride-2-ethylhexyl acrylate copolymer was prepared in 100% yield by using the recipe given in Table 19.

2. Suspension Graft Copolymerization of Vinyl Pyridine

Vinyl pyridine-grafted polyolefins [229] having improved dyeability were prepared with >0.02 wt% based on the monomer of a perester catalyst and >0.1 wt% based on the monomer of a reducing agent promoter selected from lower-valent salts of multivalent metals, hydrosulfite, or alkali metal formaldehyde sulfoxylate. Thus, the polypropylene–styrene–vinylpyridine-graft copolymer prepared in the presence of 1 wt% sodium hydrosulfite and 0.5 wt% *tert*-butyl 2-ethyl perhexanoate at 90°C was melt-spun into fibers

Table 19 Typical Recipe: Suspension Polymerization of Vinyl Chloride-2-ethylhexyl Acrylate Copolymer^a

Ingredients	Amount (g)
Water	70
Vinyl chloride	28.5
2-Ethylhexyl acrylate	1.5
Fluoronic F-68	0.3
Lupersol-11 (t-butyl peroxy-pivalate)	0.06
NaHSO ₃	0.5
CuCl ₂ ·2H ₂ O (0.00039% with respect to the monomer)	

^aPolymerization at 61°F.

which were dyed to a light-fast wash-resistant deep red shade with Capracyl Red G.

E. Monosaccharide as the Reductant

Suspension Polymerization of Vinyl Chloride

A process for the bulk or suspension polymerization of vinyl chloride in the presence of a redox catalyst system consisting of a peroxyester and a monosaccharide or carboxylic acid esters of monosaccharide was described by Gaylord [230]. The monosaccharides which were used as reductants include pentoses and hexoses wherein the carbonyl group is either an aldehyde or ketone; that is, polyhydroxy aldehydes commonly referred to as aldoses and polyhydroxy ketones commonly referred to as ketoses.

Representative monosaccharides or reducing sugars include arabinose, xylose, lyxose, ribose, glucose, mannose, allose, galactose, tallose, altrose, idose, fructose, and sorbose. The preferred concentration of peroxyester is generally between 0.5% and 1% by weight of the vinyl chloride. The peroxyester/reductant mole ratio is generally 1/0.1–1. The preferred temperature for the suspension polymerization was in the 20–60°C range and the weight ratio of monomer and water was about 2/1.

Although the peroxyester–monosaccharide or peroxyester–monosaccharide–carboxylic acid ester catalyst system is useful in the bulk and suspension polymerization of vinyl chloride, the redox system may also be used in the copolymerization of vinyl chloride with vinylidene chloride, vinyl acetate, and other monomers which undergo copolymerization with vinyl chloride.

F. Metal Mercaptides as Reductant

Gaylord et al. [231] described the bulk or suspension polymerization of ethylenically unsaturated monomers, particularly vinyl chloride, using a catalyst system consisting of a monomer-soluble peroxyester or diacyl peroxide and a reducing agent which is a stannous or antimony(III) mercaptide.

The peroxygen compound/reductant mole ratio was about 1/0.1–1. The concentration of peroxyester was about 0.05–1% by weight of the vinyl halide monomer. The concentration of both peroxygen compound and reductant may be reduced by the addition of complexing agents which contain suitable functional groups. Alternatively, the addition of complexing agents increases the rate of polymerization at a given concentration of peroxygen compound and reductant.

The rate of decomposition of a peroxygen compound such as *t*-butyl peroxyoctoate in the presence of a stannous or antimony(III) mercaptide is

decreased in the presence of vinyl chloride, presumably due to the formation of a complex between the reductant and the monomer. However, when a complexing agent containing carbonyl functionality (e.g., a ketone, lactone, carboxylic acid, or carboxylic ester) is present, the complex formation is decreased and the rate and extent of decomposition of the peroxygen compound increases, even in the presence of the monomer. The increased rate and extent of decomposition of a peroxyester or diacyl peroxide in the presence of the complexing agent is accompanied by an increase in the rate and extent of polymerization of vinyl chloride.

The complexing agents which may be used in the process of the present invention are organo-soluble and contain carbonyl groups or phosphorus-oxygen linkages. Thus, ketones, carboxylic acids and esters, and phosphate esters are effective complexing agents. The latter may be saturated or unsaturated, cyclic or acyclic, branched or linear, substituted or unsubstituted.

G. Ascorbic/Isoascorbic Acid or Esters as Reductant

Ascorbic acid has been used extensively as a sole reducing agent or in combination with cupric, ferrous, or ferric salts for the polymerization of vinyl chloride in the presence of water-soluble catalysts including hydrogen peroxide [232–235], potassium persulfate [236], cumene hydroperoxide [237], acetyl cyclohexanesulfonyl peroxide [238], and a mixture of hydrogen peroxide and acetyl cyclohexanesulfonyl peroxide [239].

Ascorbic acid has also been used as a complexing agent in the polymerization of vinyl chloride [240] in the presence of a diacyl peroxide and various water-soluble metal salts. Similarly 6-O-polmitoyl-L-ascorbic acid has been used as a reducing agent in the polymerization of vinyl chloride in the presence of hydrogen peroxide [241] and methyl ethyl ketone peroxide [242].

Suspension Polymerization of Vinyl Chloride

Gaylord [243] has described the bulk or suspension polymerization of vinyl chloride using a catalyst system consisting of a monomer-soluble peroxyester or diacyl peroxide as oxidant and a 6-O-alkanoyl-L-ascorbic acid as a reducing agent.

Bulk or suspension polymerization may be carried out at temperatures in the 20–60°C range. Gaylord [244] has also described the use of isoascorbic acid as the reducing agent in combination with a peroxygen compound as the catalyst system for the suspension polymerization of vinyl chloride.

Table 20 Polymerization of Vinyl Chloride at 50°C

Reductant	t-BPOT (wt%)	Time (hr)	Conversion %
Ascorbic acid	0.3	8.5	40.5
	0.1	8.5	20.0
Isoascorbic acid	0.1	8.5	70.5
	0.1	16.0	70.5
	0.05	16.0	40.0

A comparison of the results obtained with ascorbic acid and isoascorbic acid, in the suspension polymerization of vinyl chloride at 50°C, in the presence of t-butyl peroxyoctoate (t-BPOT) at a peroxyester/reductant mole ratio of 2/1 is given in Table 20. The use of isomeric 6-O-alkanoyl-D-ascorbic acid has been found to result in a significantly higher rate of polymerization, permitting the use of lower concentrations of peroxyester to achieve faster reaction.

VI. HYDROPEROXIDES

Generally, hydroperoxides are derivatives of hydrogen peroxide, with one hydrogen replaced by an organic radical:



Hydroperoxide chemistry had its heyday in the decade 1950–1960, following the firm establishment of these compounds as reactive intermediates in the autoxidation of olefins. Afterward, many reports regarding vinyl polymerization involving hydroperoxide alone or coupled with a suitable reducing agent have appeared in the literature.

A. Sulfur Dioxide as Reductant

There are many reports on the use of SO₂ as the reductant to initiate the polymerization. For example, Polish workers [245] studied the emulsion polymerization of the styrene–SO₂ system using cumene and pinene hydroperoxide. Gomes and Lourdes [246] investigated the liquid SO₂–cumene hydroperoxide system. Ghosh et al. used the SO₂ in combination with heterocyclic compounds by pyridine, tetrahydrofuran, and N-N'-dimethylformamide for photopolymerization [247–249] as well as aqueous polymerization [250].

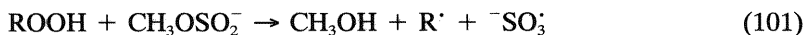
Mazzolini et al. [251–254] reported the organic hydroperoxide–SO₂ redox pair and a nucleophilic agent to polymerize vinyl chloride in bulk at subzero temperatures. Patron and Moretti [255] have also reported on the bulk polymerization of vinyl chloride using the same type of system at 20°C.

The decomposition of organic hydroperoxides by the action of SO₂ depends on the reaction medium; for example, cumyl hydroperoxide (CHP) is quantitatively decomposed into phenol and acetone if the reaction is carried out in an anhydrous weakly nucleophilic or non-nucleophilic medium (e.g., CCl₄, CH₃CN, CH₃CH₂Cl, CH₂=CHCl). This type of decomposition, which proceeds through an ionic mechanism without formation of radicals, can also be obtained [256,257] with perchloric acid, ferric chloride in benzene, and sulfuric acid. It is, therefore, inferred that SO₂ behaves as a strong acid toward the decomposition of CHP in anhydrous, weakly nucleophilic or non-nucleophilic solvents.

For a redox reaction to take place, according to the Lewis theory of acids and bases, it is necessary that the reductant (SO₂) acts as a base toward the oxidant (hydroperoxide), to allow the transfer of electrons from the former to the latter [258]. The condition is fulfilled by the addition to the reaction medium of a strongly nucleophilic agent N[−] (e.g., OH[−]) in order to transform the SO₂ into the conjugate base NSO₂[−]. When water is added to the system hydroperoxide–SO₂ and the concentration of the former increases, the absorbance at 272 mμ, characteristic of phenol, diminishes, while a new absorbance maximum, ranging between 237 and 255 mμ, emerges due to a mixture of 1-methylstyrene (3%), acetophenone (60%), and cumyl alcohol (37%). When water is added to the system hydroperoxide–SO₂ in an organic medium, a situation analogous to the emulsion polymerization by hydroperoxide and SO₂ is induced [259]. This demonstrates the possibility of switching the mechanism of reaction between hydroperoxide and SO₂ in an essentially organic medium from an ionic mechanism to a radical one, thus offering a way for the initiation of vinyl polymerization at low temperature.

According to Mazzolini et al. [251], the kinetic expressions for the continuous bulk polymerization of vinyl chloride by the hydroperoxide–SO₂ nucleophilic agent may be as follows:

Production of radicals:



and $d(\text{R}^\cdot)/dt = 2K_d(\text{ROOH})(\text{CH}_3\text{OSO}_2^-)$, where K_d is the velocity constant for the reaction of radical production.

Initiation of polymerization:



where M is vinyl chloride monomer and

$$\frac{d(M\cdot)}{dt} = K_a(R\cdot)(M) \quad (103)$$

where K_a is the velocity constant for monomer addition to primary radicals.

Propagation:



and

$$-\frac{d(M)}{dt} = K_p(M\cdot)(M) \quad (105)$$

where K_p is the velocity constant for the propagation reaction.

Termination:



$$-\frac{d(M\cdot)}{dt} = 2K_t(M\cdot)^2 \quad (107)$$

where K_t is the velocity constant for the combination reaction.

Under stationary conditions (input = output + reaction amount), the balance for the catalyst will be

$$F_0(C)_0 = F(C) + K_d(C)(S)V \quad (108)$$

where

F_0 = feed rate of all liquid streams to reactor, volume per unit time

F = output rate of the liquid fraction at overflow from reactor, volume per unit time

$(C)_0$ = hydroperoxide concentration in liquid feed

(C) = hydroperoxide concentration in reactor (or in reactor overflow)

(S) = concentration of compound $CH_3OSO_2^-$ in reactor (or in reactor overflow)

V = volume occupied by liquid phase in reactor

At sufficient dwell time and $(ROSO_2^-)/(CHP)$ molar ratios, $F(C)$ is negligible if compared to $F_0(C)_0$ and $K_d(C)(S)V$. As the catalyst decomposition approaches completion, an expression for (C) can thus be assumed:

$$(C) = \frac{F_0(C)_0}{K_d(S)V} \quad (109)$$

The balance for the monomer is

$$F_0(M)_0 = F(M) + K_p(M')(M)V \quad (110)$$

$(M)_0$ (monomer concentration in feed) and (M) (monomer concentration in liquid phase of overflow) being equal for a bulk polymerization, the monomer conversion can be expressed as

$$c = \frac{F_0 - F}{F_0} \quad (111)$$

or from the previous equation $c = K_p(M')V/F_0$.

The balance for (M') is

$$2fK_d(C)(S)V = F(M') + 2K_t(M')^2V \quad (112)$$

where f is the efficiency of initiating radicals (i.e., the fraction of radicals taking part in polymer chain initiation).

The term $2fK_d(C)(S)V$ can be assumed to be equal to $2f(C)_0F_0$. $2K_t(M')^2V$ is equal to twice the number of macromolecules formed per unit time. Both can be experimentally estimated. $F(M')$ appears to be negligible if compared to $2fK_d(C)(S)V$ and $2K_t(M')^2V$. Then, the above equation becomes

$$2K_t(M')^2 = 2fK_d(C)(S) \quad (113)$$

or substituting the value of (C) ,

$$2K_t(M')^2 = \frac{V}{2fF_0(C)_0} \quad (114)$$

Then, the conversion can be expressed as

$$C = \left(\frac{K_p}{K_t^{1/2}} \right) f^{1/2} (C)_0^{1/2} V^{1/2} F_0^{-1/2} \quad (115)$$

for conversion, not exceeding about 20%, V can be assumed as

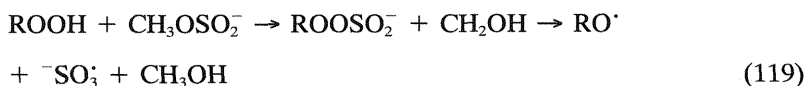
$$V = V_0(1 - c) \quad (116)$$

thus, V_0/F_0 being the conventional dwell time, Q , a final equation may be written as

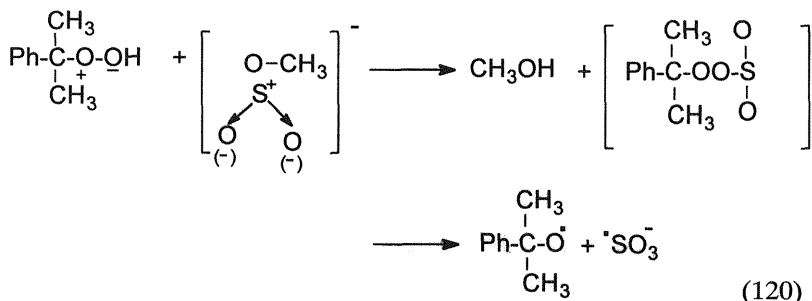
$$\frac{c}{(1 - c)^{1/2}} = \left(\frac{K_p}{K_t^{1/2}} \right) f^{1/2} (c)_0^{1/2} Q^{1/2} \quad (117)$$

In other words, the conversion is proportional to the square root of the hydroperoxide concentration and the dwell time.

The following mechanism can be proposed for the radical decomposition of the hydroperoxide by SO_2 and nucleophilic agent:



or



The oxycumyl radical may further decompose into 1-methylstyrene, acetophenone, and cumyl alcohol, or the radical itself, its fragments (CO_3^\cdot , OH^\cdot), or radicals derived from chain transfer reactions may initiate polymerization. The ${}^-\text{SO}_3$ radical is easily identified as an end group in the polymer chain. The rate-determining step for the whole catalytic reaction appears to be the formation of the complex (I), as indicated by the fact that an asymptotic limit for the polymerization rate is reached only when the $(\text{CH}_3\text{OSO}_2^-)/(\text{CHP})$ ratio is in considerable excess over the stoichiometric ratio of 1.

Bulk Polymerization of Vinyl Chloride

During the bulk polymerization of vinyl chloride [251], when cumyl or *tert*-Bu hydroperoxides and SO_2 are used with ethers, ketones, or alcohols, sulfone groups are incorporated in the polymer chain because of copolymerization of SO_2 . When the hydroperoxides and SO_2 are used with MeO or EtO (from Na or Mg alkoxides), SO_2 copolymerization is completely suppressed, provided the MeO^-/SO_2 or EtO^-/SO_2 ratio is at least 1:1. When the feed rate of hydroperoxide is constant, the maximum monomer conversion in continuous bulk polymerization is reached when the SO_2 /hydroperoxide ratio

is $\geq 1.5:1$. The percentage conversion for the various nucleophilic agents used are presented in Table 21.

The hydroperoxide– SO_2 system reacted in the vinyl chloride monomer at -30°C . Without any nucleophilic agent, the reaction proceeds via the usual ionic path and no polymerization is detected. With the addition of alcohols, ketones, and ethers, the redox reaction is promoted and substantial quantities of polymer are formed. When weak nucleophilic agents, like ethers and ketones, are used, polymerization yields are low. Higher conversions were obtained with alcohols. The best yield was obtained by the addition of 5% methanol on the monomer weight. The polymerization rate, at constant CHP and SO_2 concentrations, approaches the maximum when the $(\text{CH}_3\text{O}^-)/(\text{SO}_2)$ ratio is at least 1, employing either sodium or magnesium methoxide at a $(\text{CH}_3\text{O}^-)/(\text{SO}_2)$ ratio of 1. The SO_2 is completely transformed into the salt of methyl sulfurous acid. The systematic polymerization study was carried out using a $(\text{CH}_3\text{O}^-)/\text{SO}_2$ ratio of 1:1 to assure complete neutralization of SO_2 and avoid its copolymerization. The syndiotacticity index was 2.1–2.2 for polymers prepared at -30°C , and 2.4–2.5 for polymers prepared at -50°C . The glass transition temperature T_g was 100°C for polymers obtained at -30°C , and 104°C for polymers obtained at -50°C .

The above-described catalytic system was also effective [251] with other vinyl monomers over wide temperature ranges. The results are given in Table 22.

Table 21 Influence of Nucleophilic Agents on Bulk Polymerization of Vinyl Chloride^a

Nucleophilic agents	% (OMW)	Conversion %
None	0.00	0.00
Acetophenone	0.60	1.90
Cyclohexanone	0.49	5.10
Acetone	0.29	1.20
Methyl ethyl ether	0.36	3.70
Ethyl ether	0.52	3.20
Methanol	0.16	6.80
Methanol	5.00	10.50
Butanol	0.36	6.00
Dimethyl amine	0.22	0.40
Dimethyl formamide	0.36	0.51

^aTemperature = -30°C ; CHP = 0.15% (OMW); SO_2 = 1.6% (OMW); nucleophilic agent as specified; addition time of catalyst components into monomer = 1 hr. Total reaction time = 2 hr. OMW = on monomer weight.

Table 22 Polymerization of Vinyl Monomers by the CHP/ $\text{SO}_2/\text{Mg}(\text{OCH}_3)_2$ Catalytic System^a

Monomer	Temp. (C)	Conversion %
Vinal acetate	-30	22.0
	-60	6.0
Vinyl formate	-30	19.0
Acrylonitrile	-30	23.0
Styrene	50	15.5
Acrylamide (30% in methanol)	-30	21.0
2-Hydroxyethyl acrylate	20	56.5
	-30	27.5
<i>tert</i> -Butylaminoethyl methacrylate	20	46.5

^aCHP = 0.25% (OMW); SO_2 = 0.2% (OMW); $\text{Mg}(\text{OCH}_3)_2$ = 0.14% (on moles). Catalyst addition time = 5 hr. Total reaction time = 5 hr. (OMW = on monomer weight).

In two other patents reported by Mazzolini et al. [252,254] for bulk polymerization of vinyl chloride, they used the same type of catalytic system as above. Thus, vinyl chloride was polymerized at -30°C in the presence of a mixture of cumene hydroperoxide or *tert*-Bu hydroperoxide, a methanolic solution of SO_2 , and a methanolic solution of NaOMe, NaOEt, or KOMe.

In another German patent, Mazzolini et al. [253] reported the low-temperature bulk polymerization of vinyl chloride in the presence of a catalyst system consisting of an organic hydroperoxide, SO_2 , and at least one alkali metal alcoholate at a $[\text{ROX}]-[\text{SO}_2]/[\text{R}'\text{OOH}]$ mole ratio of 0–0.5 and 0.005–1% mercapto compound which gave a degree of conversion $>18\%$ and a polymer with outstanding physical and chemical properties. The typical recipe for the polymerization is presented in Table 23.

Patron and Moretti [255] also reported the bulk polymerization of vinyl chloride at $>0^\circ\text{C}$ in the presence of a catalyst system consisting of an organic hydroperoxide, SO_2 , and an alcohol or metal alcoholate. A 25% conversion was obtained at 25°C . The PVC recovered had an intrinsic viscosity of 1.3 and bulk density of 0.41 g cm^{-3} . They [260] also reported the bulk polymerization of vinyl chloride by taking a mixture containing liquid vinyl chloride at -30°C and a catalyst composition containing cumene hydroperoxide, SO_2 , Na methylate, and 2-mercaptoethanol that was continuously fed to a reactor. The molar weight concentration ratio of the catalyst composition

Table 23 Typical Recipe: Bulk Polymerization of Vinyl Chloride^a

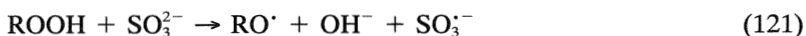
Ingredients	Amount (g hr ⁻¹)
Liquid vinyl chloride (at -30°C)	200,000
Cumene hydroperoxide	240
SO ₂	150
MeONa	136
Mercaptoethanol	60

^a36.2 kg hr⁻¹ (22.5% conversion); PVC has intrinsic viscosity 1.38 dl g⁻¹.

was (NaOME)(SO₂)/cumene hydroperoxide = 0.1. The polymerization yielded PVC with an intrinsic viscosity of 1.3 dl g⁻¹.

B. Sulfite as Reductant

The oxyacids of sulfur such as sulfite [155,199,220,253–265] form an efficient redox system in conjunction with persulfates to initiate vinyl polymerization. Sully [266] examined the Cu²⁺–SO₃²⁻ system in air. The ClO₃⁻–SO₃²⁻ system has been used in the polymerization of acrylonitrile [267,268] and acrylamide [268,269]. The KBrO₃–Na₂SO₃–H₂SO₄ system is also an effective redox initiator [270], giving rise to polymers containing strong acid end groups. All the above initiating systems have been employed in aqueous or emulsion polymerization. Reports of the use of sulfite as the reductant with organic peroxides or hydroperoxides are very few. Melacini et al. [271] have reported the bulk polymerization of acrylonitrile by redox system such as cumene hydroperoxide–dimethyl sulfite. The mechanism of initiation may be described as



These radicals take part in the initiation step. *t*-Butyl hydroperoxide (*tert*-BHP) forms free radicals with SOCl₂ in the presence of methanol which initiates the polymerization of vinyl chloride successfully [272]. It was proposed that as a first step, SOCl₂ reacts with methanol to yield methyl chlorosulfite with which *tert*-BHP reacts to form methyl *tert*-butyl peroxy sulfite, which decomposes to give free radicals.

Bulk Polymerization of Acrylonitrile

Acrylonitrile [271] polymers were prepared in bulk in high yields under controlled conditions at room temperature to 60°C in 30–90 min using radical catalysts with decomposition rate constants $>1 \text{ hr}^{-1}$. Thus, 1600 g of acrylonitrile containing 300 ppm water was kept at 50°C, and 3.2 g of cumene hydroperoxide, 23.2 g of dimethyl sulfite, and 18.1 g of magnesium methylate in 150 cm³ of MeOH were added. The conversion achieved in 15 min represented a final conversion of 77% in a continuous polymerization system.

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Photoinitiated Radical Vinyl Polymerization

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I. INTRODUCTION

When polymerizations are initiated by light and both the initiating species and the growing chain ends are radicals, we speak of *radical photopolymerization*. Molecules of appreciably high molecular weight can be formed in the course of the chain reaction. Vinyl monomers can be mostly polymerized by a radical mechanism. Exceptions are vinyl ethers, which have to be polymerized in an ionic mode. Light-induced *ionic* polymerization has been reviewed elsewhere [1–4].

Regarding initiation by light, it has to be pointed out that the *absorption* of incident light by one or several components of the polymerization mixture is the crucial prerequisite. If the photon energy is absorbed directly by a photosensitive compound, being a monomer itself or an added initiator, this photosensitive substance undergoes a homolytic bond rupture forming radicals, which may initiate the polymerization. In some cases, however, the photon energy is absorbed by a compound that itself is not prone to radical formation. These so-called sensitizers transfer their electronic excitation energy to reactive constituents of the polymerization mixture, which finally generate radicals. The radicals evolved react with the intact vinyl monomer, starting a chain polymerization. Under favorable conditions, a single free radical can initiate the polymerization of thousands of molecules. The spatial distribution of initiating species may be arranged in any desired manner.

Light-induced free-radical polymerization is of enormous commercial importance. Techniques such as curing of coatings on wood, metal and paper, adhesives, printing inks, and photoresists are based on photoinitiated radical vinyl polymerization. There are some other interesting applications, including production of laser video discs and curing of acrylate dental fillings.

In contrast to thermally initiated polymerizations, photopolymerization can be performed at room temperature. This is a striking advantage for both classical polymerization of monofunctional monomers and modern curing applications. Photopolymerization of monofunctional monomers takes place without side reactions such as chain transfer. In thermal polymerization, the probability of chain transfer is high, which brings about a high amount of branched macromolecules. Hence, low-energy stereospecific polymeric species, namely of syndiotactic configuration, may be obtained by photopolymerization. Another important use refers to monomers with low ceiling temperatures. They can only be polymerized at moderate temperatures; otherwise depolymerization dominates over polymerization. By means of photopolymerization, these monomers are often easily polymerizable. Furthermore, biochemical applications, such as immobilization of enzymes by polymerization, do also usually require low temperatures. As far as curing of coatings or surfaces is concerned, it has to be noted that thermal initiation is often not practical, especially if large areas or fine structures are to be cured or if the curing formulation is, like for dental fillings, placed in a surrounding that should rather not be heated.

Radical photopolymerization of vinyl monomers played an important role in the early development of polymerization. One of the first procedures for polymerizing vinyl monomers was the exposure of monomer to sunlight. Blyth and Hoffmann [5] reported the polymerization of styrene by sunlight more than 150 years ago.

Photocurable formulations are mostly free of additional organic solvents; the monomer, which serves as reactive diluent, is converted to solid, environmentally safe resin without any air pollution. Ultraviolet (UV) curing is often a very fast process, taking place without heating, as pointed out above. If the polymerization mixture absorbs solar light and the efficiency of radical formation is high, photocuring can be performed with no light source but sunlight. These features make photopolymerization an ecologically friendly and economical technology that has high potential for further development.

II. PHOTOINITIATION OF POLYMERIZATIONS

Photoinitiated free-radical polymerization consists of four distinct steps:

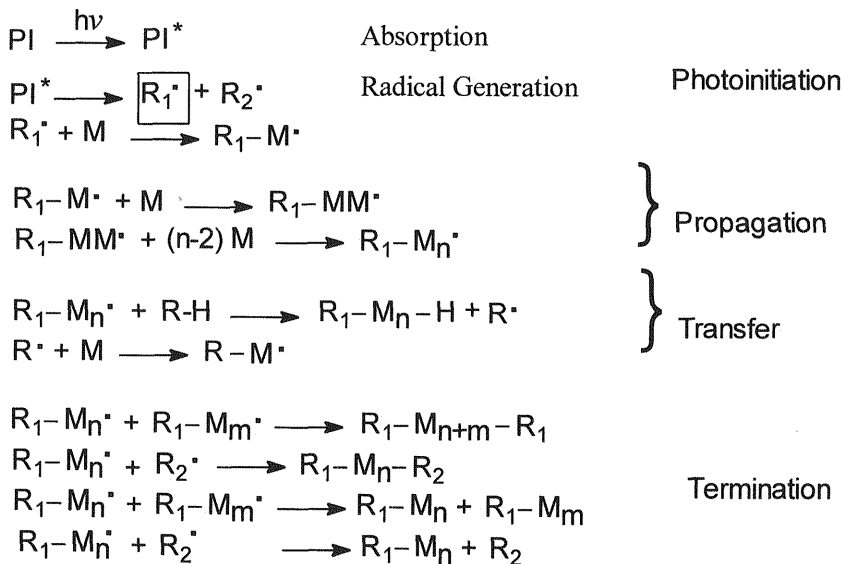
1. *Photoinitiation*: Absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light-absorbing

sensitizer to the photosensitive compound. Homolytic bond rupture leads to the formation of a radical that reacts with one monomer unit.

2. *Propagation*: Repeated addition of monomer units to the chain radical produces the polymer backbone.
3. *Chain transfer*: Termination of growing chains by hydrogen abstraction from various species (e.g., from solvent) and concomitant production of a new radical capable of initiating another chain reaction.
4. *Termination*: Chain radicals are consumed by disproportionation or recombination reactions. Terminations can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.

These four steps are summarized in Scheme 1.

Notably, the role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer, and termination are purely thermal processes; they are not affected by light. Because the genuine photochemical aspects are to be discussed in this chapter, propagation, transfer, and termination reactions are not depicted as long as it is not necessary for the understanding of a reaction mechanism. Instead, the photochemically produced initiating species are highlighted by a frame, as seen, for example, in Scheme 1.



Scheme 1

A. Absorption of Light

The absorption of light excites the electrons of a molecule, which lessens the stability of a bond and can, under favorable circumstances, lead to its dissociation. Functional groups that have high absorptency, like phenyl rings or carbonyl groups, are referred to as chromophoric groups. Naturally, photoinduced bond dissociations often take place in the proximity of the light-absorbing chromophoric groups. In some examples, however, electronic excitation energy may be transferred intramolecularly to fairly distant but easily cleavable bonds to cause their rupture.

The intensity I_a of radiation absorbed by the system is governed by the Beer–Lambert law, where I_0 is the intensity of light falling on the system, l is the optical path length, and $[S]$ is the concentration of the absorbing molecule having the molar extinction coefficient ϵ :

$$I_a = I_0(1 - e^{-\epsilon l[S]}) \quad (1)$$

If the monomer possesses chromophoric groups and is sensitive to light (i.e., it undergoes photoinduced chemical reactions with high quantum yields), one can carry out photopolymerizations by just irradiating the monomer. In many cases, however, monomers are not efficiently decomposed into radicals upon irradiation. Furthermore, monomers are often transparent to light at $\lambda > 320$ nm, where commercial lamps emit. In these cases, photoinitiators are used. These compounds absorb light and bring about the generation of initiating radicals.

B. Radical Generation

1. Radical Generation by Monomer Irradiation

Some monomers are able to produce radical species upon absorption of light. Studies on various vinyl compounds show that a monomer biradical is formed.



These species are able to react with intact monomer molecules, thus leading to growing chains. Readily available monomers which to some extent undergo polymerization and copolymerization upon UV irradiation are listed in Table 1.

However, regarding technical applications, radical generation by irradiation of vinyl monomer does not play a role due to the very low efficiency of radical formation and the usually unsatisfactory absorption characteristics.

Table 1 Photosensitive Monomers

Allyl methacrylate	Methyl methacrylate
Barium acrylate	Pentaerythritol tetramethacrylate
Cinnamyl methacrylate	Styrene
Diallyl phthalate	Tetraethylene glycol dimethacrylate
Diallyl isophthalate	Tetrafluoroethylene
Diallyl terephthalate	<i>N</i> -Vinylcarbazole
2-Ethylhexyl acrylate	Vinyl cinnamate
2-Hydroxyethyl methacrylate	Vinyl 2-fluorate
2-Hydroxypropyl acrylate	Vinyl 2-furylacrylate
<i>N,N'</i> -Methylenebisacrylamide	

2. Radical Generation by Initiators

In most cases of photoinduced polymerization, initiators are used to generate radicals. One has to distinguish between two types of photoinitiators.

Type I Photoinitiators: *Unimolecular Photoinitiators*. These substances undergo an homolytic bond cleavage upon absorption of light. The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction. The number of initiating radicals formed upon absorption of one photon is termed the quantum yield of radical formation ($\Phi_{R\cdot}$):



$$\frac{d[\dot{R}_1]}{dt} = \frac{d[\dot{R}_2]}{dt} = k[PI^*] \quad (4)$$

$$\Phi_{R\cdot} = \frac{\text{number of initiating radicals formed}}{\text{number of photons absorbed by the photoinitiator}} \quad (5)$$

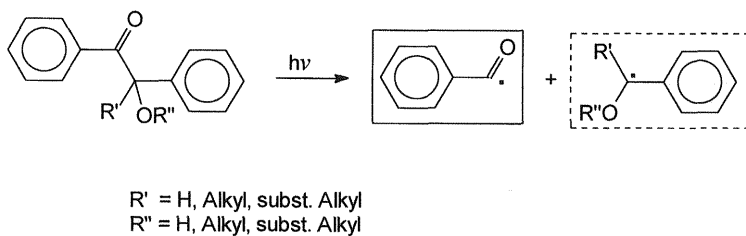
Theoretically, cleavage-type photoinitiators should have a $\Phi_{R\cdot}$ value of 2 because two radicals are formed by the photochemical reaction. The values observed, however, are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These routes include physical deactivation such as fluorescence or nonradiative decay and energy transfer from the excited state to other, ground-state molecules, a process referred to as quenching. The reactivity of photogenerated radicals with polymerizable monomers is also to be taken into consideration. In most initiating systems, only one in two radicals formed adds to the monomer, thus initiating polymerization. The other radical usually undergoes either combination or disproportionation. The initiation efficiency of photogenerated radicals (f_p) can be calculated by

$$f_p = \frac{\text{number of chain radicals formed}}{\text{number of primary radicals formed}} \quad (6)$$

The overall photoinitiation efficiency is expressed by the quantum yield of photoinitiation (Φ_p) according to

$$\Phi_p = \Phi_R \cdot x f_p \quad (7)$$

Regarding the energy necessary, it has to be said that the excitation energy of the photoinitiator has to be higher than the dissociation energy of the bond to be ruptured. The bond dissociation energy, on the other hand, has to be high enough in order to guarantee long-term storage stability. The majority of Type I photoinitiators are aromatic carbonyl compounds with appropriate substituents, which spontaneously undergo α -cleavage, generating free radicals according to reaction (8). The benzoyl radical formed by the reaction depicted is very reactive toward the unsaturation of vinyl monomers [6].



(8)

The α -cleavage, often referred to as Norrish Type I reaction [7] of carbonyl compounds, starts from the initiator's triplet state, which is populated via intersystem crossing. Notably, the excited triplet states are usually relatively short-lived, which prevents excited molecules from undergoing side reactions with constituents of the polymerization mixture. Although triplet quenching by oxygen can, in most cases, be neglected due to the short lifetime of the triplet states, quenching by monomer sometimes plays a role. However, this refers exclusively to monomers with low triplet energies, like styrene ($E_T = 259 \text{ kJ mol}^{-1}$ [8]).

If the absorption characteristics of a cleavable compound are not meeting the requirements (i.e., the compound absorbs at too low wavelengths), the use of sensitizers (S) with matching absorption spectra is recommended. Sensitizers absorb the incident light and are excited to their triplet state. The triplet excitation energy is subsequently transferred to the photoinitiator, which forms initiating radicals. This process has to be exothermic; that is, the sensitizers triplet energy has to be higher than the triplet energy level of the initiator. Through energy transfer, the initiator is excited and undergoes the same reactions of radical formation as if it were excited by direct ab-

sorption of light. The sensitizer molecules return to their ground state upon energy transfer; they are, therefore, not consumed in the process of initiation.



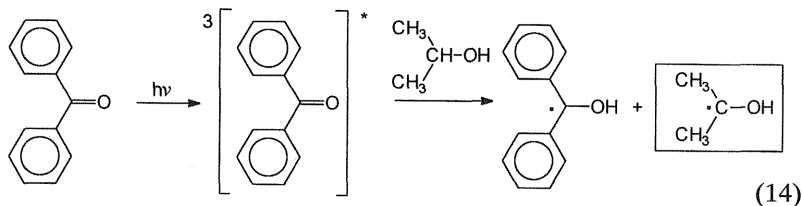
Type II Photoinitiators: Bimolecular Photoinitiators. The excited states of certain compounds do not undergo Type I reactions because their excitation energy is not high enough for fragmentation; that is, their excitation energy is lower than the bond dissociation energy. The excited molecule can, however, react with another constituent of the polymerization mixture—the so-called coinitiator (COI)—to produce initiating radicals. In this case, radical generation follows second-order kinetics.



$$\frac{d[\dot{R}_1]}{dt} = \frac{d[\dot{R}_2]}{dt} = k[PI^*][COI] \quad (13)$$

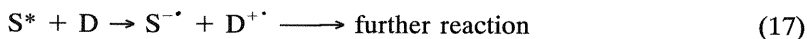
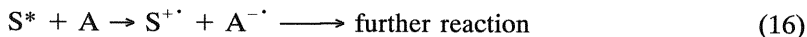
There are two distinct pathways of radical generation by Type II initiating systems:

- I. *Hydrogen abstraction* from a suitable hydrogen donor: As a typical example, the photoreduction of benzophenone by isopropanol is depicted. Bimolecular hydrogen abstraction is limited to diaryl ketones [7]. From the point of view of thermodynamics, hydrogen abstraction is to be expected if the diaryl ketone's triplet energy is higher than the bond dissociation energy of the hydrogen atom to be abstracted.



- II. Photoinduced *electron transfer reactions* and subsequent fragmentation: In electron transfer reactions, the photoexcited molecule, termed the sensitizer for the convenience, can act as either electron donor or electron acceptor according to the nature of the sensitizer and coinitiator. Fragmentation yields radical anions and radical cations, which are often not directly acting as initiating

species themselves but undergo further reactions, by which initiating free radicals are produced.



The electron transfer is thermodynamically allowed, if ΔG calculated by the Rehm–Weller equation (18) [9] is negative.

$$\Delta G = F \left[E_{1/2}^{\text{ox}} \left(\frac{D}{D^{+\cdot}} \right) - E_{1/2}^{\text{red}}(A/A^{-\cdot}) \right] - E_s + \Delta E_c \quad (18)$$

where

F = Faraday constant

$E_{1/2}^{\text{ox}}(D/D^{+\cdot})$, $E_{1/2}^{\text{red}}(A/A^{-\cdot})$ = oxidation and reduction potential of donor and acceptor, respectively

E_s = singlet-state energy of the sensitizer

ΔE_c = coulombic stabilization energy

Electron transfer is often observed for aromatic ketone–amine pairs and always with dye/coinitiator systems. The photosensitization by dyes is dealt with in detail in Section V.

III. TYPE I PHOTOINITIATORS

A. Aromatic Carbonyl Compounds

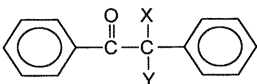

1. Benzoin Derivatives

Benzoin and its derivatives are the most widely used photoinitiators for radical polymerization of vinyl monomers. As depicted in reaction (8), they undergo α -cleavage to produce benzoyl and α -substituted benzyl radicals upon photolysis.

The importance of these photoinitiators derives from the following: They possess high absorptions in the far-UV region ($\lambda_{\text{max}} = 300\text{--}400$ nm, $\epsilon_{\text{max}} \geq 100\text{--}200$ L mol⁻¹ cm⁻¹), high quantum efficiencies for radical generation [10], and a relatively short-lived triplet state [11] (Table 2).

Regarding the photochemistry of benzoin derivatives, starting from excited triplet states populated after intersystem crossing, Norrish Type I bond scission is the main chemical reaction occurring under various experimental conditions [21–25]. As a consequence of this bond cleavage, benzoyl and ether radicals are formed. In the absence of the monomer, hydrogen abstraction takes place, leading to benzaldehyde, benzil, and pinacol

Table 2 Various Benzoin Derivatives: Quantum Yields of α -Scission (Φ_α), Triplet Energies (E_T), and Triplet Lifetimes (τ_T)

		X	Y	Φ_α	E_T (kJ mol ⁻¹)	τ_T (10 ⁻⁹ sec)	Ref.
H	H	—	302	125	12		
OH	H	0.87	308	0.83	13–15		
OCH ₃	H	0.44	300	<0.1	13–15		
OCH(CH ₃) ₂	H	0.33	—	—	16		
OCH(CH ₃)C ₂ H ₅	H	0.30	—	—	16		
OC ₆ H ₅	H	0.39	304	0.17	13, 14		
OCOCH ₃	H	0.33	—	20	13, 14		
OH	C ₆ H ₅	0.10	—	—	16		
CH ₃	CH ₃	0.44	306	6	12, 17		
OCH ₃	OCH ₃	0.57	278	<0.1	16, 18–20		
		0.11			16		

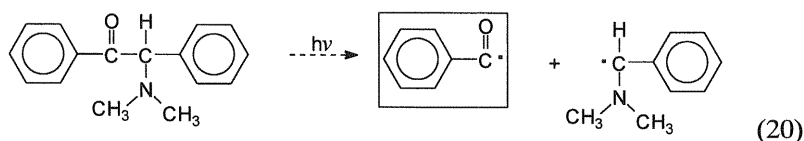
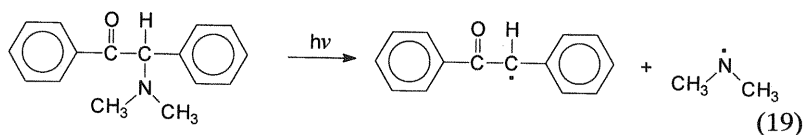
derivatives [21–23]. The reactivity of benzoyl and benzyl ether radicals were found to be almost the same, provided the concentration of radicals is low and that of the monomer high. On the other hand, if the concentration of radicals is high and that of the monomer low, benzoyl radicals are more reactive toward monomer molecules present than the ether radicals [10,24,26].

The photoinduced α -cleavage reaction is not or is only slightly affected by triplet quenchers including styrene, owing to the short lifetime of the excited triplet state [27]. This circumstance makes benzoin photoinitiators particularly useful for industrial applications involving the styrene monomer.

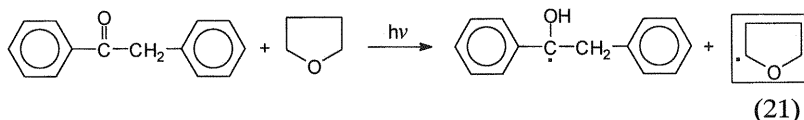
Regarding practical applications, it has to be mentioned that benzoin derivatives are storable for only a limited time at ambient temperature; that is, they slowly but steadily decompose during storage. Thermally, benzylic hydrogen atoms are abstracted, giving rise to benzyl radicals and various subsequent decomposition products. Several benzoin derivatives, like benzil ketals or metholyl benzoin derivatives (*vide ante*), are more thermally stable.

A few benzoin derivatives decompose by photofragmentation mechanisms other than Norrish Type I. For example, α -halogen acetophenones [28], oxysulfonyl ketones [29], and sulfonyl ketones [30] sufficiently undergo β -cleavage upon UV irradiation and may be used for initiation. α -Dimethylamino-substituted benzoin undergoes both α -cleavage and β -pho-

to elimination, the latter being the dominant process [14]. Because the radicals formed according to reaction (19) are not reactive toward the monomer and the quantum yield of α -cleavage [reaction (20)] is low (~ 0.04), these derivatives are not suitable photoinitiators.



Another benzoin derivative, desoxybenzoin, undergoes α -scission with rather low quantum yields, too. However, it becomes an efficient initiator when utilized together with a hydrogen donor, such as tertiary amine or tetrahydrofuran. In this case, initiating radicals are generated by hydrogen abstraction with comparatively high yields [31,32]:



When used in conjunction with onium salts, various methylol functional benzoin ethers are efficient cationic photoinitiators [33,34]. One important advantage of methylol benzoin derivatives (Table 3) is their relatively high thermal stability. See Table 3.

Table 3 Methylol Benzoin Derivatives

Methylolbenzoin [35,36]	Methylolbenzoin propyl ether [35]	Methylolbenzoin, 1-octosulfonic ester [37–39]

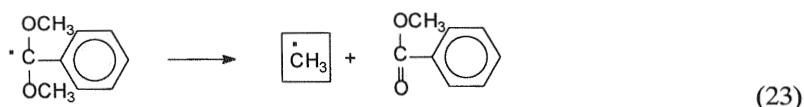
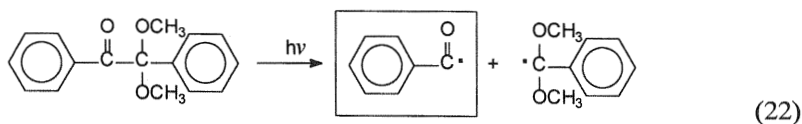
In the case of methylolbenzyl sulfonic acid esters, the initiation efficiency could be considerably enhanced by adding lithium salt to the formulations [38]. This effect has been explained in terms of the formation of the sulfonic acid ester's lithium salt. This salt migrates toward the surface of the coating and thereby forms a shield preventing oxygen from diffusing into the inner zones of the coating.

2. Benzilketals

Benzilketals are another important class of photoinitiators (Table 4) developed for free-radical vinyl polymerization. Benzilketals exhibit higher thermal stability than benzoin compounds due to the absence of thermally labile benzylic hydrogen. The most prominent member of this class is the commercially used 2,2-dimethoxy-2-phenylacetophenone (DMPA). This initiator shows an excellent efficiency in photopolymerizations and is, at the same time, easy to synthesize. Other benzilketals are also suitable initiators but do not reach the price performance ratio of DMPA.

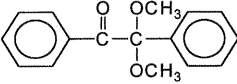
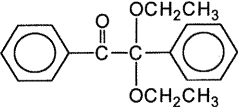
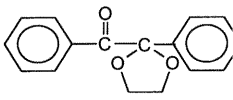
Like benzoin ethers, benzilketals undergo α -cleavage whereby a benzoyl radical and a dialkoxybenzyl radical is formed. Whereas the benzoyl radicals are, as explained earlier, vigorously reacting with olefinic bonds of vinyl monomers, dialkoxybenzyl radicals were found to be of low reactivity. Actually, one of seven dialkoxy benzyl radicals formed is found to be incorporated into the polymer chain during the photopolymerization of methyl methacrylate initiated by DMPA [41]. However, to what extent this portion of dialkoxy benzyl groups is caused by termination rather than initiation remains unclear.

Dimethoxybenzyl radicals undergo a fragmentation, yielding methyl radicals [42–44], which act as additional initiating species in radical vinyl polymerization [18,45]:



Mechanistic studies [18,46–48a] based on electron spin resonance (ESR) and ENDOR analysis revealed that the fragmentation reaction depicted in reaction (23) is a fast two-photon process, provided high-intensity light

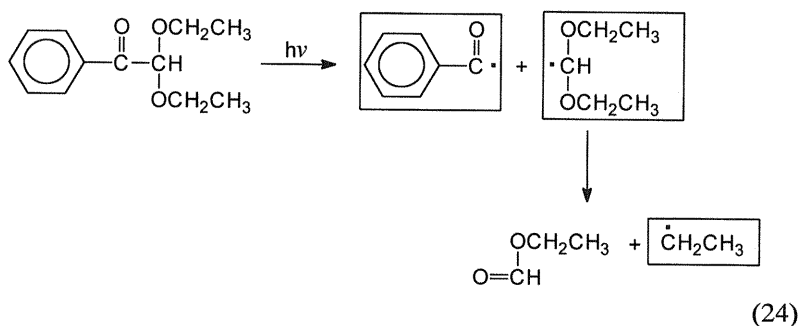
Table 4 Benzilketals for Photopolymerization

		
2,2-dimethoxy-2-phenylacetophenone (DMPA) [16,18–20]	2,2-diethoxy-2-phenylacetophenone	benzilglycolketal (BGK) [16,39a,40]

sources (pulsed lasers) are used for photolysis. On the other hand, relatively low-intensity light gives rise to a slower, thermal fragmentation.

3. Acetophenones

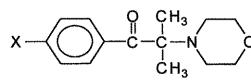
α -Substituted acetophenones are another important class of photoinitiators used in various applications of free-radical polymerizations [42,49–51]. These initiators exhibit excellent initiator properties, especially in micellar solutions [52]. The most prominent example of this class of photoinitiators is the commercially available α,α -diethoxyacetophenone (DEAP); furthermore 1-benzoylcyclohexanol and 2-hydroxy-2-methyl-1-phenylpropanone are initiators with good properties. In addition to high efficiency, the pros of acetophenones include high storage stability and little tendency toward yellowing. Regarding photochemistry, both Norrish Type I and Norrish Type II bond ruptures were evidenced [45]. However, only the α -cleavage (Norrish Type I) gives initiating radicals: benzoyl radicals directly formed upon the light-induced α -cleavage and ethyl radicals, generated in a subsequent thermal fragmentation reaction.

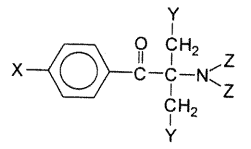


4. α -Aminoalkylphenones

α -Aminoalkylphenones (Table 5) have recently been developed for the use in pigmented photopolymerizations. These compounds possess better ab-

Table 5 α -Aminoalkylphenones for Photopolymerization: Quantum Yields of α -Scission (Φ_α), Triplet Energies (E_T), and Triplet Lifetimes (τ_T)

					
X	Φ_α	E_T (kJ mol ⁻¹)	τ_T (10 ⁻⁹ s)		
H	1	—	1		
CH ₃ O	1	273	0.4		
CH ₃ S	0.88	256	10		
(CH ₃) ₂ N	0.014	265	2000		

					
X	Y	Z	Φ_α	E_T (kJ mol ⁻¹)	τ_T (10 ⁻⁹ sec)
H	C ₆ H ₅	CH ₃	1	—	1
Morpholine	C ₆ H ₅	CH ₃	0.22	—	1700
Morpholine	CH ₂ =CH—	CH ₃	>0.9	—	1500
Morpholine	CH ₂ =CH—	—C ₂ H ₄ OC ₂ H ₄ —	0.07	—	80

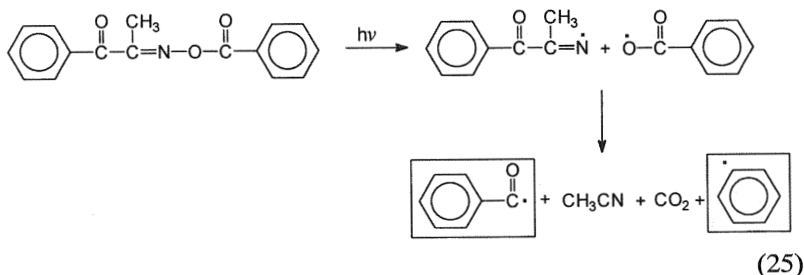
Source: Ref. 53, p. 157.

sorption characteristics than many other aromatic ketone photoinitiators and are, therefore, quite amenable to practical applications where irradiation at longer wavelengths is desired. There is no doubt that α -aminoalkylphenones undergo α -cleavage to yield initiating benzoyl radicals and other carbon-centered radicals [54,55,277]. By means of thioxanthone as a triplet sensitizer, the sensitivity of the initiating formulation can be extended to the near-UV or even visible region of the spectrum [56–58]. Recently, the ammonium group containing benzoin ethers have turned out to be efficient, water-soluble photoinitiators in the polymerization of trimethylolpropane triacrylate [59].

5. O-Acyl- α -oximino Ketones

O-Acyl- α -oximino ketones are known to undergo cleavage with high quantum efficiency [60] and have been used as photoinitiators for acrylates and unsaturated polyesters [28,60–62]. Besides benzoyl radicals, phenyl radicals

are produced in a secondary reaction. Both radical types are reactive in initiation. The most prominent example of these initiators is *O*-benzoyl- α -oximino-1-phenyl-propane-1-one, the reaction of which is illustrated in reaction (25).



Although these compounds absorb more strongly in the near-UV than most of the other aromatic photoinitiators, their use as photoinitiators is limited, as they are thermally not very stable. The relatively weak N–O bond dissociates both photochemically and thermally at moderate temperatures.

6. Acylphosphine Oxide and Its Derivatives

Acylphosphine oxide and acylphosphonates with different structures have been used as photoinitiators for free-radical-initiated photopolymerization (see Table 6).

Long-wavelength absorption characteristics make these compounds particularly useful for the polymerization of TiO_2 -pigmented formulations containing acrylate- or styrene-type monomers and of glass-fiber-reinforced polyester laminates with reduced transparency [68–73,275]. These initiators are thermally stable up to $\sim 180^\circ\text{C}$ and no polymerization takes place when the fully formulated systems are stored in dark. Moreover, very little yellowing occurs in coatings cured with acylphosphine oxides. With respect to the storage of curing formulations and the curing itself, it has to be taken into account that acylphosphine oxides may react with water, alcohols, or amines, which leads to the cleavage of the C–P bond [73]. By introducing bulky groups in the position of the benzoyl group, the solvolysis is significantly slowed down. Furthermore, these substituents seem also to be able to increase the proneness to α -scission (see Table 6).

Extensive investigations on the photochemistry of acylphosphine oxides revealed that they do undergo α -cleavage with fairly high quantum yields [64]. Furthermore, it was found that the phosphonyl radicals formed are highly reactive toward vinyl monomers, as can be seen in Table 7, where

Table 6 Phosphonates for Photopolymerization: Quantum Yields of Intersystem Crossing (Φ_T), α -Scission (Φ_α), and Triplet Lifetimes (τ_T)

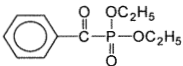
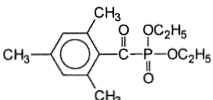
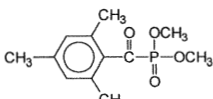
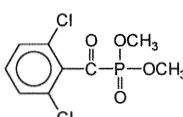
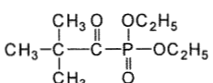
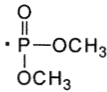
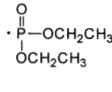

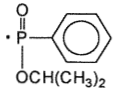
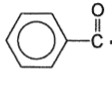
Structure	Φ_T	Φ_α	τ_T (10^{-9} sec)	Ref.
	0.9	0.03	24	63, 64
	0.6	0.3	—	65
	0.6	0.3	—	65
	0.5	0.2	—	63
	0.6	0.3	30	64, 66, 67

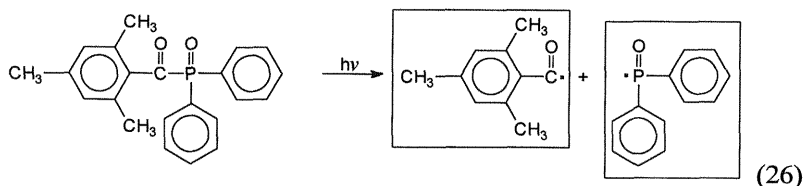
Table 7 Bimolecular Rate Constants ($1 \text{ mol}^{-1} \text{ sec}^{-1}$) of the Reaction of Phosphonyl and Benzoyl Radicals with Various Monomers in Cyclohexane at 20°C

					
St	2.2×10^8	2.5×10^8	8×10^7	4.5×10^7	$<2 \times 10^5$
AN	5.8×10^6	2.6×10^6	1.8×10^6	2.0×10^7	$<2 \times 10^4$
MA	1.7×10^7	1.6×10^7	1.3×10^7	2.1×10^7	

Note: St = styrene; AN = acrylonitrile, MA = methylacrylate.

Source: Ref. 66.

rate constants of radicals generated from photoinitiators with various monomers are compiled.



Notably, dialkoxyphosphonyl radicals are highly reactive toward monomers. For carbon-centered benzoyl radicals, significantly lower rate constants are detected. The excellent reaction efficiency of phosphonyl radicals is attributed to the high electron density at the phosphorus atom and the pyramidal structure of the radicals providing more favorable steric conditions for the unpaired radical site to react with monomers.

7. α -Hydroxy Alkylphenones

α -Hydroxy alkylphenone is another photoinitiator containing benzoyl groups that has found practical application in many vinyl polymerizations [74–76]. This initiator has both a high light sensitivity and good thermal stability. Furthermore, coatings prepared using α -hydroxy alkylphenone do show only very little yellowing, which makes these compounds particularly suitable for clear coatings [19]. Another striking advantage is that α, α' -dilalkyl hydroxyphenones are liquid at room temperature and are of relatively low polarity. Therefore, they are easy to dissolve in nonpolar curing formulations [77–81].

Regarding the photochemistry of α -hydroxy alkylphenones, α -scission is the dominating reaction starting from the first excited triplet state (see Table 8). Although the reactivity of benzoyl radicals toward monomers is now doubtful (*vide ante*), the question of whether the hydroxyalkyl radical able to initiate polymerization is not entirely elucidated. However, for 1-hydroxycyclohexylphenylketone-initiated polymerization [see reaction (27)] of methyl 2-*tert*-butyl acrylate, it has been shown by analysis of photolysis products that hydroxyalkyl radicals add to the double bond of the monomer [53].

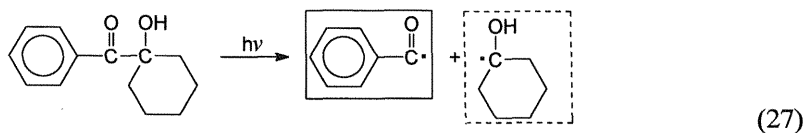
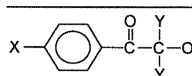

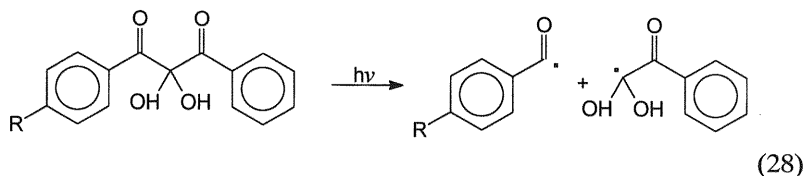


Table 8 Various α -Hydroxy Alkylphenones: Quantum Yields of α -Scission (Φ_α), Triplet Energies (E_T), and Triplet Lifetimes (τ_T)

					
X	Y	Φ_α	E_T (kJ mol ⁻¹)	τ_T (10 ⁻⁹ sec)	Ref.
H	CH ₃	0.2–0.3	298	30	82, 83
CH(CH ₃) ₂	CH ₃	0.2–0.3	—	50	82
H			281	—	19, 41
OCH ₃	CH ₃	0.38	298	12	84
OCH ₂ COOH	CH ₃	0.1	—	55	85
OCH ₂ CH ₂ OH	CH ₃	0.06	—	120	85
SCH ₂ CH ₂ OH	CH ₃	≤0.4	—	10,000	85
N(CH ₃) ₂ ^a	CH ₃	0.011	264	3,300	84

Recently, various derivatives of dibenzoyldihydroxy methane have been used for free-radical polymerization of acrylic monomers [86]. Photocalorimetric and real-time infrared (IR) investigations gave evidence that these compounds are excellent photoinitiators.

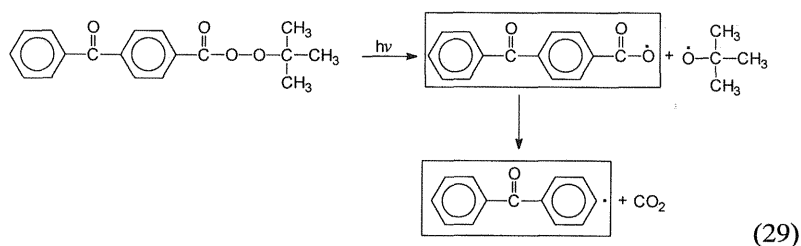


B. Peroxy Compounds

The use of peroxides as initiators for vinyl polymerization is not new, and articles describing their ability have been published and reviewed [87,88]. Peroxides contain two adjacent oxygen atoms with overlapping lone-pair orbitals. The average bond energy of the O–O linkage is about 143 kJ mol⁻¹; that is, this bond is relatively weak.

In early investigations, hydrogen peroxide has been used as an initiator for the photoinduced free-radical polymerization of acrylonitrile [89–91]. However, hydrogen peroxide only absorbs weakly, and solubility problems are unavoidable, especially if apolar monomers are to be polymerized.

Organic peroxides such as benzoyl peroxide are well known as thermal initiators. Their use as photoinitiators in free-radical polymerization is hampered by their low absorption at wavelengths above 300 nm and their thermal instability. For photopolymerization, chromophoric groups absorbing at $\lambda > 320$ nm were attached to either benzoyl peroxide [92] or perbenzoic acid ester [93–97]. In these systems, the excitation energy is transferred from the light-absorbing aromatic carbonyl moieties to the perester moieties, which undergo homolytical bond scission. Although organic peroxy compounds are quite efficient in initiating vinyl polymerization, they are scarcely used as photoinitiators because of their high thermal instability. Formulations containing peroxides may be stored for a very short time only.



C. Azo Compounds

Although diarylazo compounds are stable toward light, alkylazo compounds readily dissociate upon irradiation to give free radicals. The use of a perfluoro derivative of azomethane, namely hexafluoro azomethane, as a photoinitiator of vinyl polymerization is well known [98–100]. This compound can be photolyzed to give $\text{F}_3\text{C}\cdot$ radicals that do, in the presence of the excess vinyl monomer, initiate polymerizations.

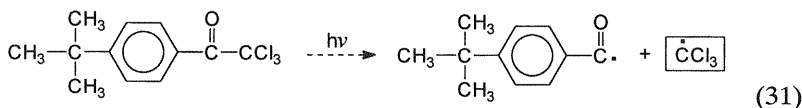
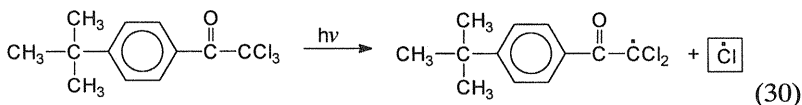
Regarding azonitriles, the famous thermal initiator 2,2'-azobisisobutyronitrile (AIBN) has also shown some potential for photochemical initiation. It was used to polymerize vinyl acetate [102–104], styrene [103,105], vinyl chloride [106], methyl methacrylate [103], and acrylonitrile [107]. Also of certain interest as photoinitiators for vinyl polymerization are α -azobis-1-cyclohexanecarbonitrile [108–110] and 1',1'-azodicyclohexanecarbonitrile [111].

However, the relatively low absorbency of azo compounds has prevented their widespread use as photoinitiators. Furthermore, they are easily thermally decomposable, which reduces the lifetime of fully formulated curing mixtures.

D. Halogens and Halogen-Containing Compounds

In a number of early investigations, halogens such as chlorine [112–114], bromine [112,115,116], and iodine [112,117] have been employed as photoinitiators for vinyl polymerization. It is assumed that the initiation involves the formation of a complex of halogen with the monomer. This complex absorbs the incident light and decomposes to yield initiating free radicals [116]. Moreover, the direct addition of photolytically formed halogen radicals could account for the initiation. In practical applications, halogens are not in use as photoinitiators, which is certainly due to inconveniences arising from handling, storage, and disposal.

Because the bonds between carbon and halogen atoms are relatively weak (except for C–F), halogenated compounds have some potential as photoinitiators. Halogenated acetophenone derivatives, such as α,α,α -trichloro-4-*tert*-butylacetophenone, were shown to undergo both β - and α -scission; the first process was found to dominate [28].



The chlorine radicals formed according to reaction (30) are very reactive: They either react with monomer molecules, thus initiating growth of a chain, or abstract hydrogen from various components of the polymerization mixture.

IV. TYPE II PHOTINITIATORS

A. Aromatic Ketone–Coinitiator System

Photolysis of aromatic ketones, such as benzophenone, in the presence of hydrogen donors, such as alcohols, amines, or thiols, leads to the formation of a radical stemming from the carbonyl compound (ketyl-type radical in the case of benzophenone) and another radical derived from the hydrogen donor [see reaction (14)]. Provided vinyl monomer is present, the latter may initiate a chain polymerization. The radicals stemming from the carbonyl compound are usually not reactive toward vinyl monomers due to bulkiness and/or the delocalization of the unpaired electron.

Apart from benzophenones, thioxanthone, anthraquinones, ketocoumarins, and some 1,2-diketones are used in conjunction with coinitiators for initiating vinyl polymerizations. As explained earlier, both electron and hydrogen transfer can bring about radical formation in the case of Type II photoinitiators. In many systems, both processes occur.

Because the initiation is based on a bimolecular reaction, Type II photoinitiators initiate generally slower than Type I photoinitiators. These systems are, therefore, more sensitive to the quenching of excited triplet states, which are the reactive precursors of light-induced chemical changes for carbonyl compounds. Indeed, quenching by monomers with a low triplet energy (e.g., styrene or *N*-vinyl carbazol) or by oxygen is often observed and may lead to relatively low curing rates (see Table 9).

In view of applications, the selection of the coinitiator is undoubtedly of great importance. Amines are used primarily because of their high efficiency and the relatively low price. Excited carbonyl triplet states are usually by two or three orders of magnitude more reactive toward tertiary amines than toward alcohols or ethers. Trialkylamines are very efficient but are sometimes disregarded for their strong odor. Alkanolamines are efficient and less smelly, but they lack good thermal stability and may also cause yellowing of the final polymer material. Aromatic amines have good initiating properties but are slightly more expensive.

1. Benzophenones

Hydrogen abstraction by the excited triplet manifold of benzophenone, which is populated with quantum yields close to unity, from tertiary amines (*N*-methyl diethanolamine) is depicted in reactions (32) and (33) [118].

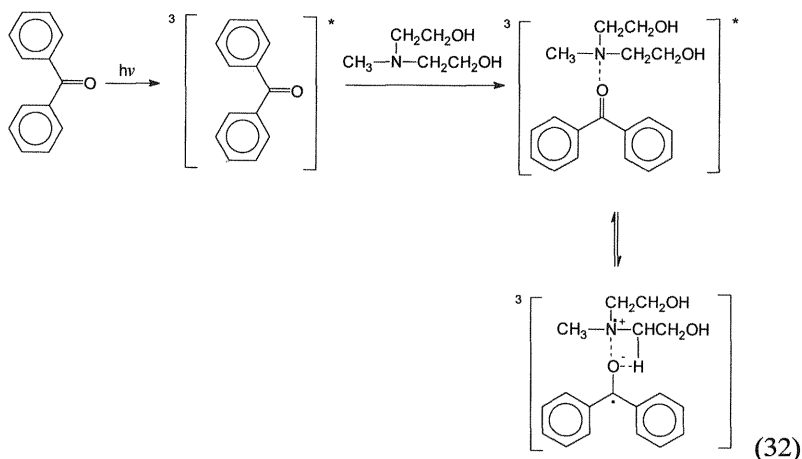
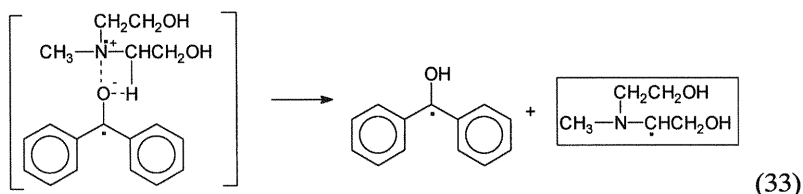


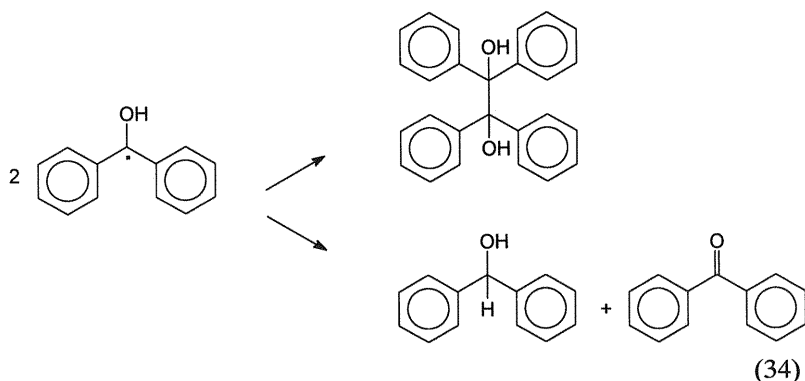
Table 9 Rate Constants for the Quenching of Benzophenone Triplet States by Monomer

Monomer	k_q (L mol ⁻¹ sec ⁻¹)
Styrene	3.3×10^9
<i>N</i> -Vinyl pyrrolidone	3.6×10^8
Methyl methacrylate	6.9×10^7
Methyl acrylate	7.5×10^6

Source: Ref. 125.

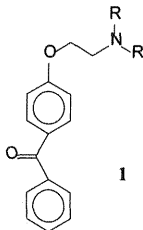
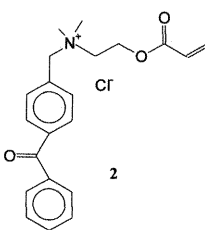
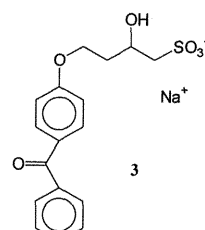
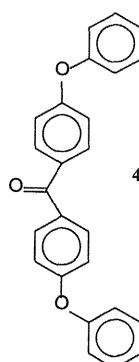


The carbon-centered radical stemming from the amine is able to initiate free-radical polymerizations of suitable monomers. α -Aminoradicals are especially suitable for the polymerization of acrylates [119] and are less efficient in styrene polymerization, which is explainable in terms of triplet quenching by styrene. In Table 9, rate constants for triplet quenching by various monomers are compiled. The ketyl radicals add due to resonance stabilization and, for steric reasons, only scarcely to olefinic double bonds but instead undergo recombination and disproportionation reactions, as shown in reaction (34).



Furthermore, they may act as chain terminators in the polymerization leading

Table 10 Miscellaneous Benzophenone-Type Photoinitiators

 <p>1</p>	 <p>2</p>	 <p>3</p>	 <p>4</p>
[129,136]	[131–133,135]		[134,137]

to ketyl moieties incorporated into polymer chains and relatively short chains [120].

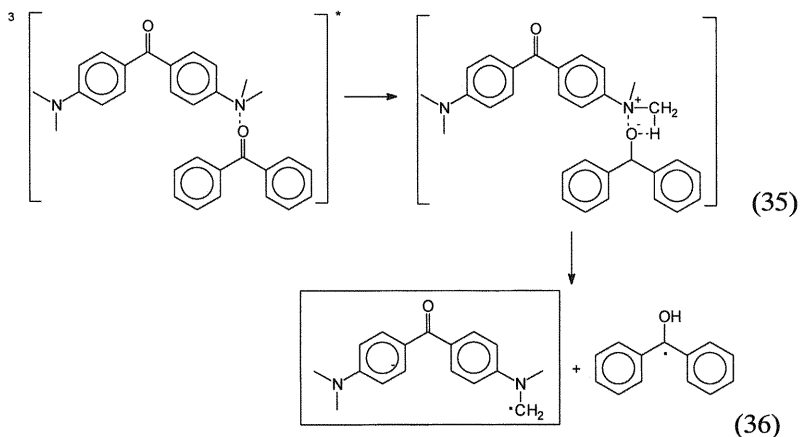
In order to avoid chain termination by ketyl radicals, additives such as onium salts [121–123] or certain bromocompounds [124] have turned out to be useful. These additives react with the ketyl radicals, thus suppressing chain termination. In the case of onium salts, phenyl radicals, which initiate polymerizations instead of terminating growing chains, are produced by the interaction of ketyl radicals with salt entities. Thus, the overall effect of these additives is an enhancement in polymerization rate.

Recently, benzophenone-based initiators with hydrogen donating amine moieties covalently attached via an alkyl spacer were introduced as photoinitiators for vinyl polymerization [101,126–130] (see **1**, Table 10). Although also following the general scheme of Type II initiators, the initiation is a monomolecular reaction, as both reactive sites are at the same molecule. Hydrogen transfer is suspected to be an intramolecular reaction. The ionic derivatives (**2** and **3**) shown in Table 10 are used for polymerization in the aqueous phase [131–133]. With 4,4'-diphenoxybenzophenone (**4** in Table 10) in conjunction with tertiary amines, polymerization rates that are by factor of 8 higher than for benzophenone were obtained [134].

2. Michler's Ketone

Michler's ketone, 4,4'-bis(dimethylamino)benzophenone, is another efficient hydrogen-abstraction-type photoinitiator that possesses both chromophoric aromatic ketone and tertiary amine groups in its structure. It absorbs much

stronger light of 365 nm than does benzophenone. Michler's ketone may undergo photoinduced hydrogen abstraction from ground-state molecules, but with a relatively low efficiency [138]. However, in most cases it is used in conjunction with benzophenone and serves as a hydrogen donor. The mechanism involves electron transfer in the exciplex formed and subsequent hydrogen abstraction [reactions (35) and (36)] [139].

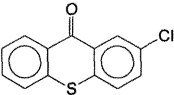
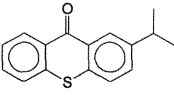
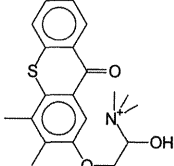
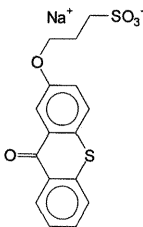


It is noteworthy that the combination of Michler's ketone and benzophenone gives a synergistic effect: This system is more efficient in forming initiating radicals than are the two components in conjunction with amines. A disadvantage of Michler's ketone is the yellow color—coatings cured with this ketone possess. It prevents a utilization of the highly efficient benzophenone–Michler's ketone system in white pigmented formulations. Moreover, regarding Michler's ketone, there is a suspicion of carcinogenicity.

3. Thioxanthenes

Thioxanthenes (Table 11) in conjunction with tertiary amines are efficient photoinitiators [140] with absorption characteristics that compare favorably with benzophenones; absorption maxima are in the range between 380 and 420 nm ($\epsilon = 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$), depending on the substitution pattern. The reaction mechanism has been extensively investigated by spectroscopic and laser flash photolysis techniques [64,141–143]. It was found that in conjunction with tertiary amines, reactions similar to that of benzophenone–amine systems take place.

Table 11 Thioxanthone Derivatives for Photoinitiation

			
[142]	[144]	[145,146]	

The most widely used commercial derivatives are 2-chlorothioxanthone and 2-isopropylthioxanthone. Furthermore, ionic thioxanthone derivatives have been developed, which may be employed for water-based curing formulations [145,146]. A great advantage is that thioxanthenes are virtually colorless and do not cause yellowing in the final products.

As for other Type II initiating systems, quenching by the monomer has to be taken into account, provided monomers with low triplet energies are used. Thus, the bimolecular rate constants of the reaction of various thioxanthenes with styrene are between 3×10^9 and $6 \times 10^9 \text{ L mol}^{-1} \text{ sec}^{-1}$. For acrylonitrile, for example, values in the range between 4×10^5 and $4 \times 10^6 \text{ L mol}^{-1} \text{ sec}^{-1}$ are found, indicating very little quenching [64].

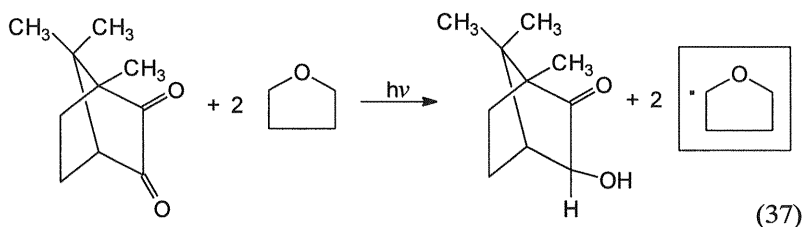
Interestingly, when *N*-ethoxy-2-methylpyridinium salt is added to the mixture consisting of a monomer (methyl methacrylate) and thioxanthone, a significant enhancement of the polymerization rate is detected [147]. This effect has been attributed to a reaction of ketyl radicals stemming from thioxanthone with the pyridinium salt, which leads to the generation of initiating ethoxy radicals.

4. Ketocoumarins

In conjunction with tertiary amines, ketocoumarins act as highly efficient Type II photoinitiating systems [148–151]. The spectral sensitivity of this system can be tuned to various wavelengths of the visible part of the spectrum by selection of suitable substituents. Moreover, the substitution pattern determines whether the coumarin acts as electron donor or as electron acceptor. 3-Ketocoumarins with alkoxy substituents in the 5- and 7-position show good absorption in the near-UV and are excellent electron acceptors. Regarding coinitiators, alkylaryl amines are most suitable.

B. Benzil and Quinones

Benzil and quinones, such as 9,10-phenanthrene quinone and camphor quinone in combination with hydrogen donors can be used as photoinitiators both in the UV and visible region [120,152,153]. Photopolymerization of methyl methacrylate using benzil was elaborately studied by Hutchinson et al. [120]. They have observed a threefold increase in the polymerization rate when a hydrogen-donating solvent such as THF was used in the system, indicating the importance of hydrogen abstraction.



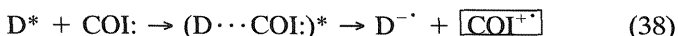
Amines, such as dimethylaniline and triethylamine, are also used as coinitiators for free-radical polymerizations [154,155]. In these cases, initiating radicals are supposedly generated through exciplex formation, followed by proton transfer. The low order of toxicity of camphor quinone and its curability by visible light makes such systems particularly useful for dental applications [152,156,157]. Noteworthy is that the reactivity is relatively low, owing to a comparably low efficiency in hydrogen-abstraction reactions. This circumstance has prevented the use of quinones in other applications.

V. DYE-SENSITIZED INITIATION

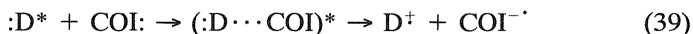
Most of the photoinitiators described up to now are sensitive to light at wavelengths below 400 nm. This enables an easy processability, as the sun and many artificial sources of light do overwhelmingly emit light of higher wavelengths and, therefore, photoinduced reactions before the intended initiation by UV light may be kept at a low level. However, if the strong emission of mercury lamps or the sun in the visible region of the spectrum is to be used, photoinitiating systems that absorb visible light are required. Such systems often involve dyes as light-absorbing chromophores. Numerous photoinitiated free-radical polymerizations using dyes have been described and reviewed by several authors [158–162]. Initiating radicals are generated by photoinduced electron transfer. Energy transfer is not thermodynamically favorable in these systems due to low excitation energies of

dyes. Depending on the nature of the dye involved, two distinct mechanisms are to be considered:

1. Electron transfer from coinitiator to the excited, *photoreducible dye* molecule yields radical cations of the coinitiator and radical dye anions. The former can initiate the polymerization. In many cases, however, initiating radicals are formed in subsequent thermal reactions. Species deriving from the dye molecule do not react with monomer molecules.



2. Electron transfer from the excited, *photooxidizable dye* to the coinitiator. In this case too, the initiating radicals stem mostly from the coinitiator.



For initiating radical polymerizations, the reaction (38) is commonly followed.

A disadvantage of many dye-containing formulations is that they lack good storage ability. This phenomenon is due primarily to the basicity of coinitiators, which can abstract hydrogen from the dye, thus leading to depletion.

A. Photoreducible Dye–Coinitiator Systems

As can be seen in Table 12, differently colored photoreducible dyes are used for sensitizing cationic polymerizations. As coinitiators, the substances in Table 13 have found application in conjunction with photoreducible dyes.

Among amine coinitiators, phenylglycidine has been reported to be particularly efficient. As depicted in reaction (40), the formation of initiating radicals is due to a thermal fragmentation reaction.

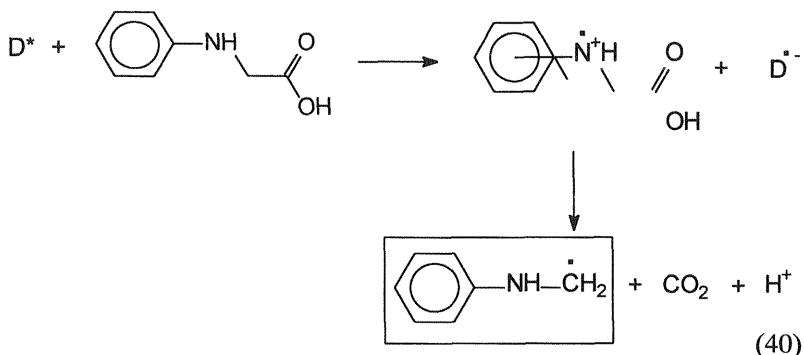
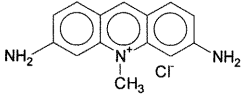
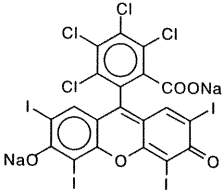
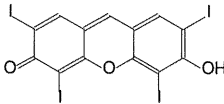
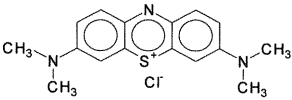
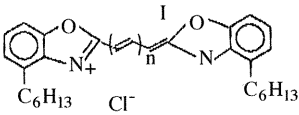
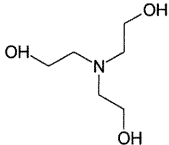
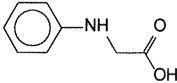
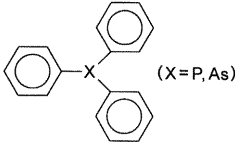
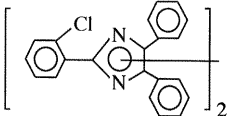


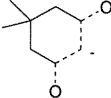
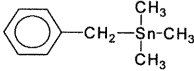
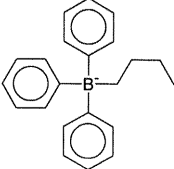


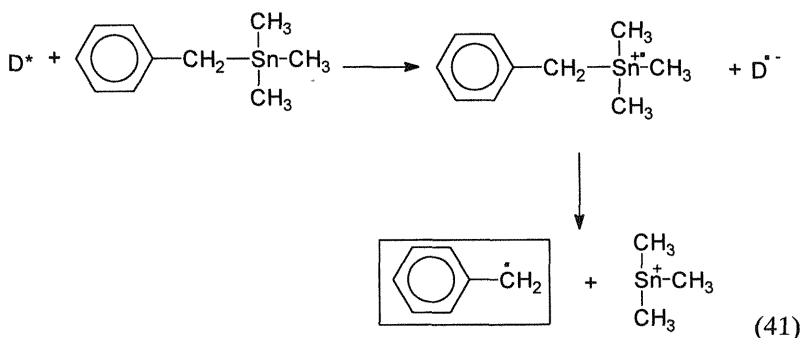
Table 12 Absorption Characteristics of Typical Photoreducible Dyes

Type	Example	λ_{\max} (nm)
Acridinium	 <p>Acriflavine</p>	460
Xanthene	 <p>Rose Bengal</p>	565
Fluorone		536
Thiazene	 <p>Polymethylene Blue</p>	645
Polymethylene	 <p>Cyanine Dye</p>	490–700, depending on n

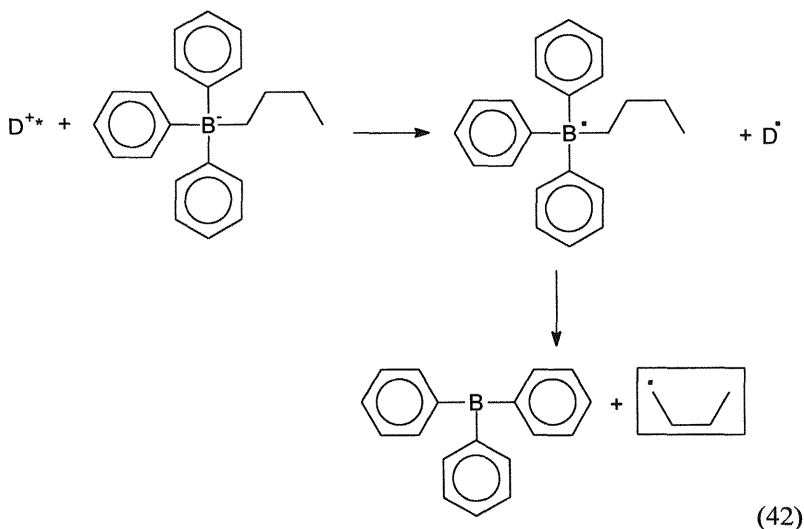
Regarding organotin compounds, it is noteworthy that although systems containing these coinitiators are not above average as far as reactivity is concerned, they are superior to many other systems based on dye sensitization for their high storage stability.

Table 13 Coinitiators for Dye-Sensitized Free-Radical Polymerization

Type	Formula	Name	Ref.
Amines		Triethanolamine	163
		<i>N</i> -Phenylglycine	164, 165
		<i>N,N</i> -dimethyl-2,6-diisopropylaniline	166, 167
	$\text{H}_2\text{N}-\text{NH}_2$	Hydrazine	168–170
Phosphines and arsines		Triphenyl-phosphine, triphenylarsine	171
Sulfinates	$\text{R}-\text{S}(=\text{O})-\text{R}'$		172–175
Heterocycles		Imidazole	176
		Oxazole	176
		Thiazole	176
Endolates		Dimedone enolate	177
Organotin comp.		Benzyltrimethylstannate	165
Borates		Triphenylmethyl borate	178–180



Borate salts are especially useful in combination with cyanine dyes. Depending on the cyanine used, there are different absorption maxima in the visible region with usually high molar extinction coefficients ($\epsilon \sim 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$). Radical formation by borate is illustrated in reaction (42).



In contrast to many other initiating systems based on dye sensitization, cyanine–borate complexes are ionic before electron transfer and are transformed into neutral species. Other systems are neutral before electron transfer and get ions thereafter.

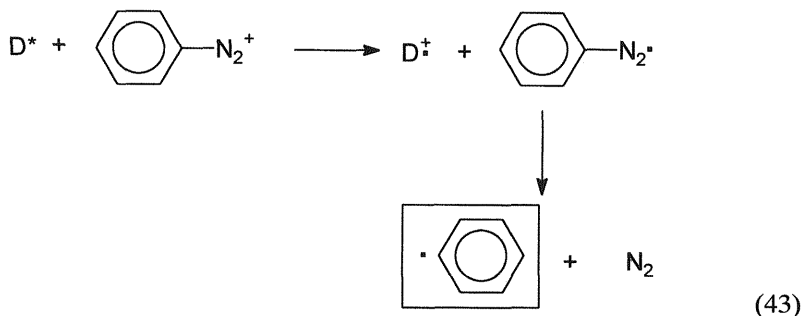
In some works, photoreducible dyes, such as acridine and xanthene, were used without adding any coinitiator for the photopolymerization of styrene, α -methylstyrene, and methyl methacrylate [181]. The initiation has

in these cases been explained in terms of electron transfer reactions between excited dye and monomer molecules.

B. Photooxidizable Dye–Coinitiator Systems

As far as photooxidizable dyes are concerned, the oxidation of dyes such as acridine or xanthene by onium salts is to be mentioned. Onium salts, like aryldiazonium, diaryliodonium, phosphonium, and sulfonium salts, are able to oxidize certain dyes. In Table 14 reduction potentials of various onium salts are depicted. Notably, the higher (more positive) the value of $E_{1/2}^{\text{red}}(\text{On}^+)$ is, the more capable is the salt to oxidize a dye.

The decomposition of diazonium salts by excited xanthene dyes (eosin, erythrosin, rhodamin B) in ethanol solution has been attributed to the oxidation of the dye [187]. These systems were employed for a photopolymerization process in which vinyl monomers [vinylpyrrolidone, bis(acrylamide)] were cross-linked by visible light [188]. The initiation is depicted as

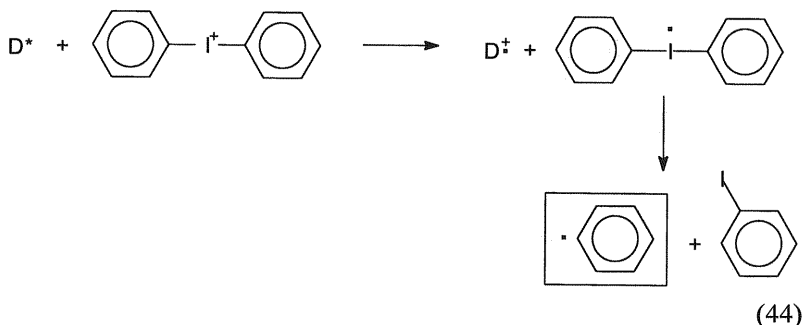


The oxidation of various dyes of iodonium salts and the use of these systems for both free-radical and ionic polymerization has been reported by

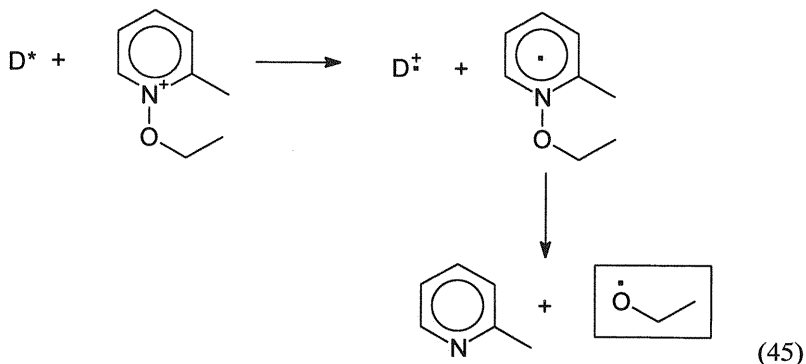
Table 14 Reduction Potentials of Onium Salt Cations, $E_{1/2}^{\text{red}}(\text{On}^+)$ in V

-1.1 [182]	-0.7 [183]	-0.5 [184]	-0.5 [184]	-0.2 [185]	0.35 [186]

several authors [161,189–191]. Although the radical-initiating species derive from the onium salt, dye radical cations are able to initiate cationic polymerizations.



Pyridinium salt has been reduced by anthracene. This reaction was utilized for the light-induced polymerization of methyl methacrylate. In this case, ethoxy radicals have been found to react with monomer molecules [147].



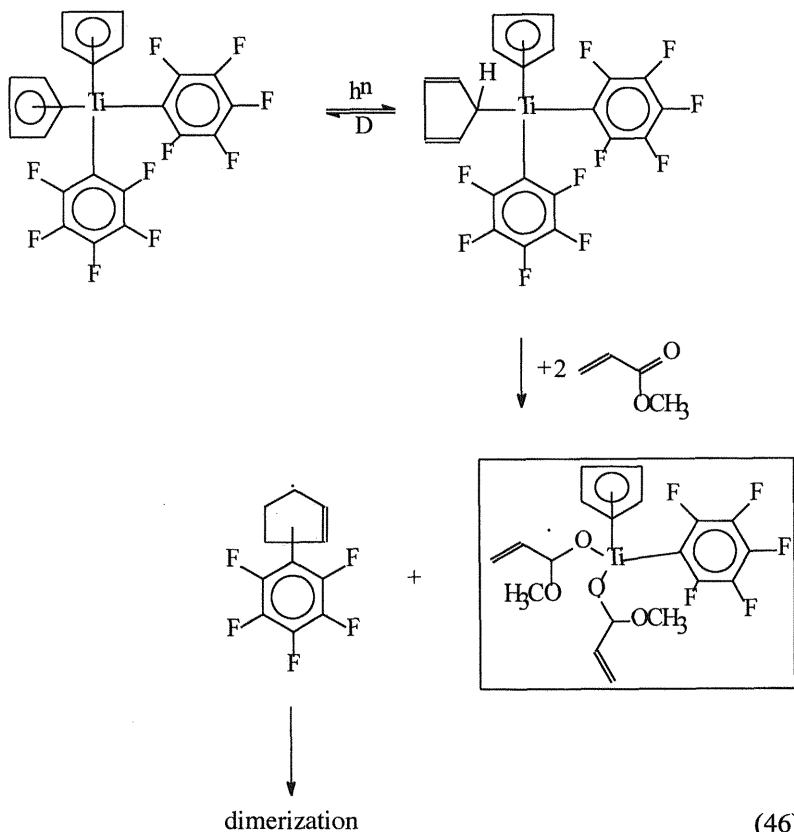
Furthermore, the photoreduction of cyanine dyes by polyhalogen-containing hydrocarbons was used for light-induced vinyl polymerization [192,193].

VI. ORGANOMETALLIC PHOTOINITIATORS

Organometallic compounds have great potential as photoinitiators—many of them have satisfactory absorption characteristics and undergo photoinduced chemical reactions, which may be utilized for initiation of polymerizations. However, the use of many organometallic compounds is hampered

by either their lack of thermal stability or their relatively high order of toxicity.

Titanocene initiators turned out to be the most attractive organometallic photoinitiators for visible-light curing [194–197,276]. Fluorinated titanocenes [see reaction (46)] are thermally stable (decomposition at $\sim 230^\circ\text{C}$) and do absorb strongly in the range between 400 and 500 nm. Furthermore, they are poisonous. The mechanism by which they initiate vinyl polymerizations has been the subject of extensive investigations [198–201]. It is assumed that the initial titanocene species undergo a photoinduced isomerization, yielding a coordinatively unsaturated and therefore highly reactive isomer with a quantum yield of nearly 1. In the presence of acylates, initiating biradicals and pentafluorophenyl-cyclopentenyl radicals are formed. The latter radical species are not prone to reactions with monomer but instead dimerize.



Apart from titanocene initiators, iron arene complexes have also been applied for light-induced radical polymerization, namely of acrylates [202–204]. Iron arene complexes were originally developed for cationic polymerization because they release acid upon irradiation. However, light-induced reactions include the formation of alkyl radicals, which may be utilized for radical initiation.

VII. MACROPHOTOINITIATORS

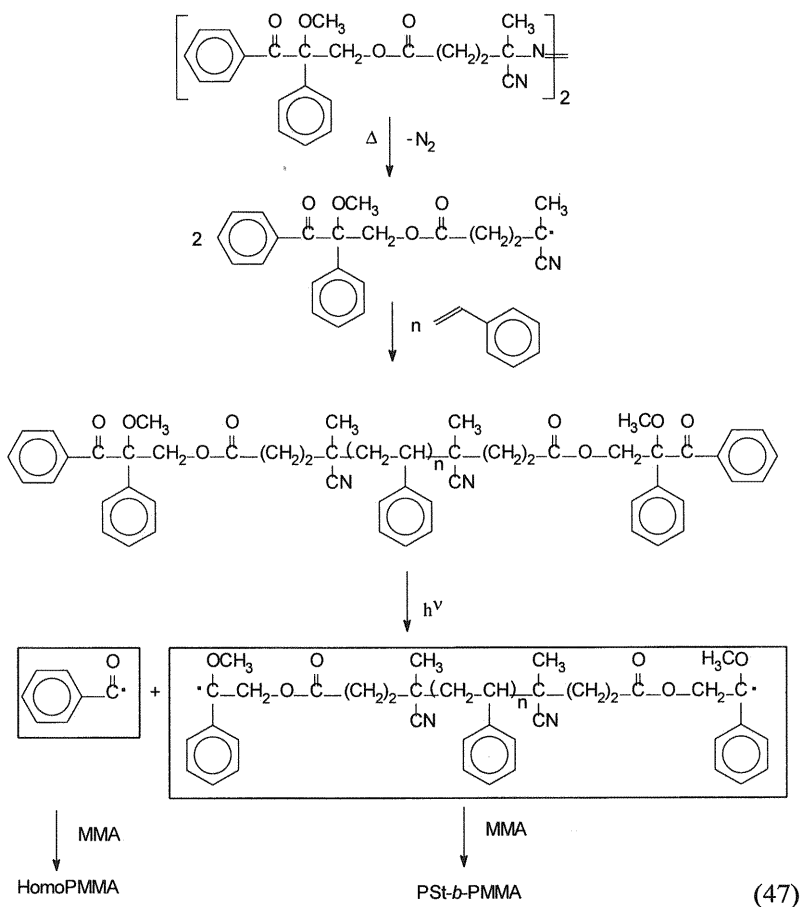
Macromolecular photoinitiators have attracted much attention in the past years. They combine properties of polymers with those of low-molecular-weight photoinitiators [205–208]. Solubility or miscibility problems, often observed with coatings containing low-molecular-weight photoinitiators, do not occur with the macromolecular ones, as polymers are easily miscible with the resin to be cured as well as the final, cured film. Moreover, odor and toxicity problems do not occur with macroinitiators, due to the low volatility of large molecules. The low migration tendency of polymeric photoinitiators and of photoproducts brings about a reduced proneness to yellowing of cured coatings. In many cases, macroinitiators were used in order to make tailor-made block or graft copolymers [209]. Besides that, photo-reactive polymers are of outstanding importance in photolithography.

A. Type I Macrophotoinitiators

As for low-molecular-weight photoinitiators, polymers that with a high quantum yield undergo homolytic bond dissociation upon irradiation are referred to as Type I photoinitiators. In many cases of Type I macrophotoinitiators, scissile moieties like benzoin derivatives or *O*-acyl- α -oximino ketones are functional groups attached to a host polymer backbone in a polymer analog reaction. Another possibility is the attachment of photosensitive groups to monomers. In this case, macrophotoinitiators are formed by polymerization or copolymerization with another monomer. A few polymers, like polysilanes, are prone to light-induced main chain scission to an extent, which enables this reaction to be used for initiating vinyl polymerizations.

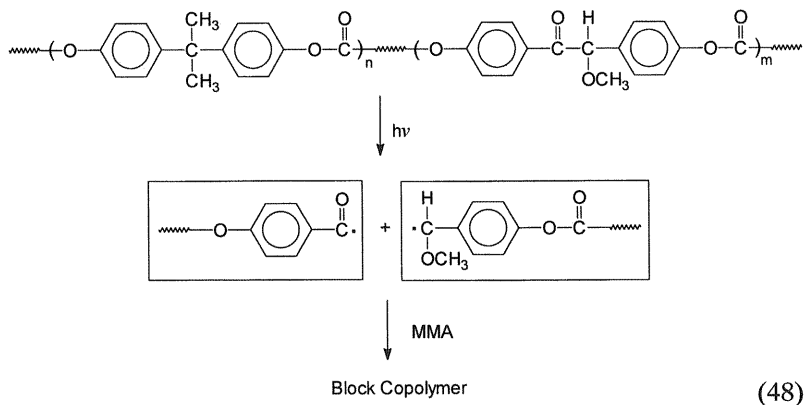
Polymers containing terminal photoactive benzoin groups have been synthesized using azo-benzoin initiators [210,211]. The thermal treatment of these initiators in the presence of styrene leads to benzoin groups at both ends of the polystyrene chain, as polystyryl radicals tend to terminate via recombination. Upon irradiation of the styrene-based photoinitiators, benzoyl and alkoxy-benzyl radicals are produced, both capable of initiating polymerizations to give mixtures of homopolymers and block copolymers [212].

Obviously, one could also use the benzoin site of the azo-benzoin initiator for a photopolymerization in the first step and activate the azo sites in a subsequent, thermal reaction [213]. However, regarding homopolymer formation, the method depicted in reaction (47) has to be given priority because benzoin groups are thermally stable, whereas azo groups may be photolytically ruptured. Benzoin-azo initiators are, furthermore, suitable for the synthesis of block copolymers with one of two monomers being cationically polymerizable [214,215].



Benzoin methyl ethers have been incorporated into a polycarbonate chain. The synthesis was achieved by polycondensing bisphenol A with phosgene in the presence of 4,4'-dihydrobenzoin methylether [216]. Irradiation of the resulting polycondensate in the presence of methyl methacrylate

resulted in block copolymer formation, as illustrated in reaction (48). Apart from methyl methacrylate, other vinyl monomers, such as ethyl methacrylate and acrylonitrile, have been polymerized by the macroinitiator [217].



Macroinitiators containing groups of benzoin type in the side chain were synthesized by several authors [13,218–233]. Some examples are summarized in Table 15. Notably, a spacer between the polymer backbone and the benzoin moiety enhances the activity of the initiator in vinyl polymerization considerably [36]. This phenomenon is attributed to an easier accessibility of reactive benzoin sites.

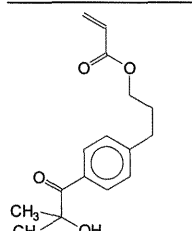
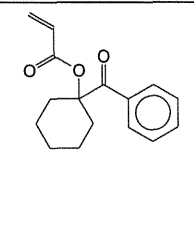
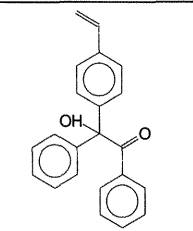
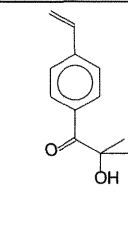
Several polymerizable monomers based on either acrylic acid or styrene-containing photodissociable groups have been developed [36, 125,278,279]. See Table 16.

These monomers may be radically homopolymerized or copolymerized with various vinyl monomers. By choosing the appropriate comonomer, one

Table 15 Side-Chain Benzoin-Type Macroinitiators

[218]	[13]	[219–220]	[221]

Table 16 Monomers-Containing Scissile Groups

 <p>[278]</p>	 <p>[125]</p>	 <p>[279]</p>	 <p>[279]</p>
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can design either hydrophobic or hydrophilic macroinitiators [223]. Macro-photoinitiators prepared from the two styrene-based monomers depicted were found to possess an activity comparable to that of efficient low-molecular-weight photoinitiators.

Polymers that possess carbonyl groups in the side chains are able to generate lateral macroradicals upon UV irradiation. The polymers depicted in Table 17 have been used as photoinitiators. Photolysis of these initiators in the presence of vinyl monomers gives both graft copolymer and homopolymer, because radicals bound to the backbone and low-molecular-weight carbonyl radicals are formed.

Copolymers containing carbonyl groups in the main chain have been used in early works as photoinitiators. These copolymers undergo main chain scission upon irradiation. In the presence of the vinyl monomer, the terminal radicals react with the monomer, initiating its polymerization. Following this method, various block copolymers (second comonomer in the block copolymer: methyl methacrylate) have been obtained. See Table 18.

Polymer-bound acyl oxime esters have also been reported to be suitable radical sources [216]. Polyesters containing acyl oxime oxides were prepared by a polycondensation reaction [230]. Irradiation of these compounds with 365 nm light in the presence of vinyl monomers (styrene) gave block copolymers.:

Table 17 Polymers with Side-Chain Carbonyl Groups

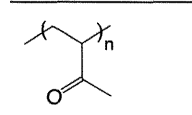
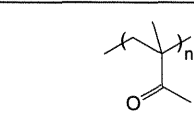
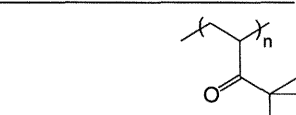
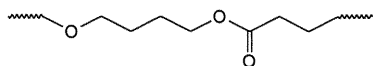
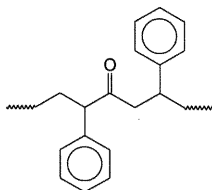
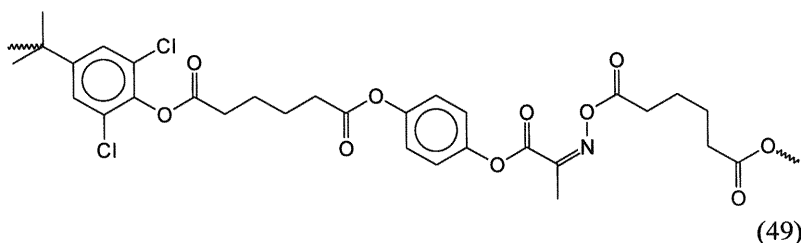
 <p>[224]</p>	 <p>[225]</p>	 <p>[225]</p>
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Table 18 Photoinitiators with In-Chain Carbonyl Groups

[226]

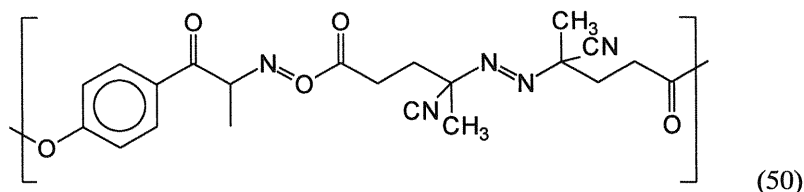


[227–229]



(49)

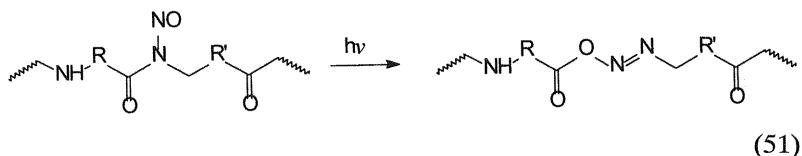
Polystyrene containing acyl oxime ester groups was synthesized using an axo-acyloxime ester bifunctional initiator [reaction (50)] [231,232]. In the first stage, the azo-acyloxime ester initiator was heated in the presence of styrene, whereby styrene polymerization is initiated by the azo sites. In a second step, the acyloxime ester sites were photochemically activated to start the polymerization of a second monomer. The striking advantage of acyloxime ester groups in macrophotoinitiators derives from the fact that upon photolysis apart from the macroradicals, two low-molecular-weight products (CH_3CN and CO_2) are formed. These photolysis products prevent the macroradicals from recombining, which leads to relatively high initiation efficiencies:



(50)

A similar effect is observed for polymeric initiators containing nitroso groups in their main chain [233]. Upon absorption of two photons, nitrogen is released and initiating macroradicals are formed, as depicted in reaction (51). Care must be taken while working with nitroso-containing macroini-

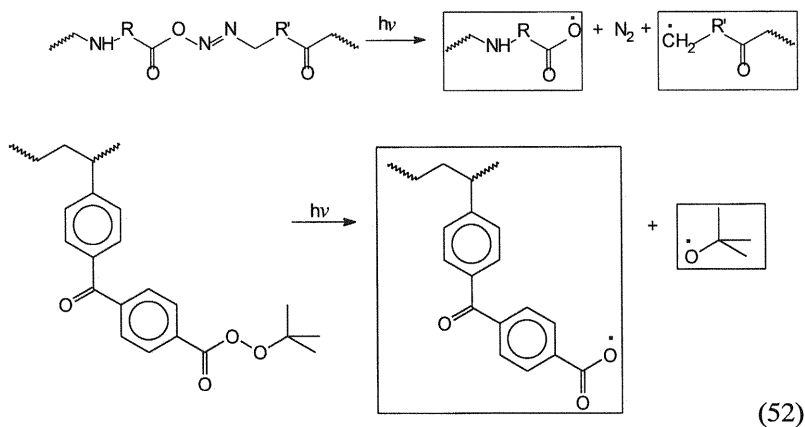
tiators, for they may decompose violently under the influence of UV light or heat [234].



Photosensitive polymers containing azo groups [235,236] or triazene groups [237] in the main chain also undergo main chain scission and evolve nitrogen upon UV irradiation. With respect to photochemistry, alkylaryl initiators are of special interest because they have better absorption characteristics than dialkyl initiators and are, on the other hand, more reactive than the respective diaryl-substituted compounds.

Various organic disulfides, including thioram disulfides, are also capable of acting as thermal and photochemical initiators for free-radical polymerization. For example, when the polymerization of styrene was initiated by tetraethylthioram disulfide, the polymer was found to contain terminal $\text{Et}_2\text{N-CS-S}$ groups. Photolyzed in the presence of vinyl monomer, these photosensitive polymers give block copolymers [238].

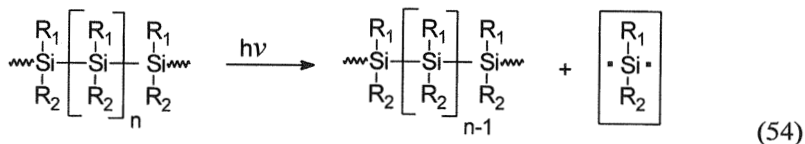
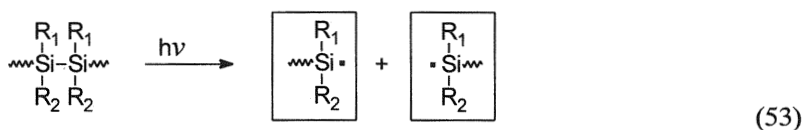
Peroxyesters with triplet photosensitizer functionalities are efficient initiators for free-radical polymerization of a monomer, provided the monomers do not quench the polymer's excited triplet state. For example, methyl methacrylate was photografted onto polystyrene containing a low fraction of peroxybenzoate [reaction (52)] [95,136]. Upon irradiation in the presence of methyl methacrylate, both homopolymer and graft copolymer was formed, as can be easily understood on the basis of reaction (52):



Polymers containing halogen atoms, especially brominated polymers, have also shown some potential in free-radical polymerization. Because the bond energy of C–X is relatively low for X being chlorine or bromine, these bonds are easily photolytically ruptured. Thus, brominated polystyrene was used to initiate the polymerization of methyl methacrylate [239,240]. Furthermore, brominated polyacrylamide and polyacrylonitrile served as a radical-generating photoactive polymer for the grafting of acrylamide and ethyleneglycol oligomers [241,242].

The curing of polysiloxane formulations by chemically attached groups of initiating Type I is of great interest. Because the cured coatings possess interesting features, such as high stability toward heat and chemicals and good flexibility, they are attractive for a number of applications [243–245]. Prepared by various synthetic strategies, polysilanes containing benzoin ether [246], benzoin acrylate [247], benzilketals [248], α,α -dialkoxyacetophenones, α -hydroxyalkylphenones [248,249], and α,α -dialkylacethophenone [250] were used as macrophotoinitiators.

Because of their high photosensitivity, polysilanes are suitable sources of free radicals [274]. These silicon-based polymers decompose upon absorption of UV light with quantum yields ranging between 0.2 and 0.97 [251], producing silyl radicals and silylene biradicals:



Polysilanes usually absorb light of wavelengths below 350 nm; changes of the organic substituents R_1 and R_2 as well as the number of silica atoms per chain, however, cause considerable alterations in the absorption characteristics [251–253]. Although radicals are formed with high yields, the initiation efficiency of polysilanes is not very high, presumably due to disproportionation reactions between the two kinds of radicals formed. However, polysilanes showed good performance in photocuring of vinyl functionalized polysiloxanes [254] and in the polymerization of several vinyl monomers [255,256]. In the latter study, upon irradiation of polysilane–vinyl copoly-

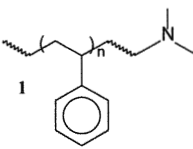
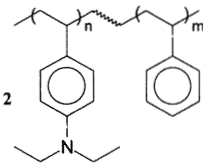
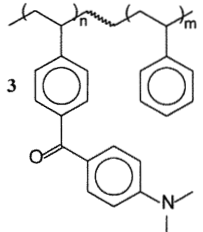
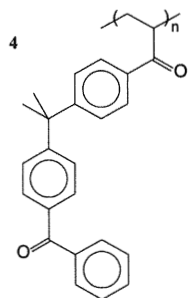
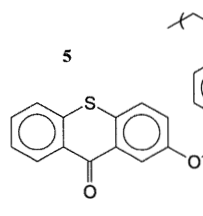
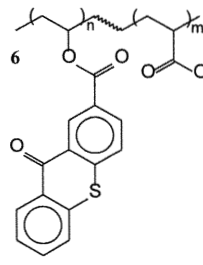
mers in the presence of a further monomer, block copolymers were synthesized [256].

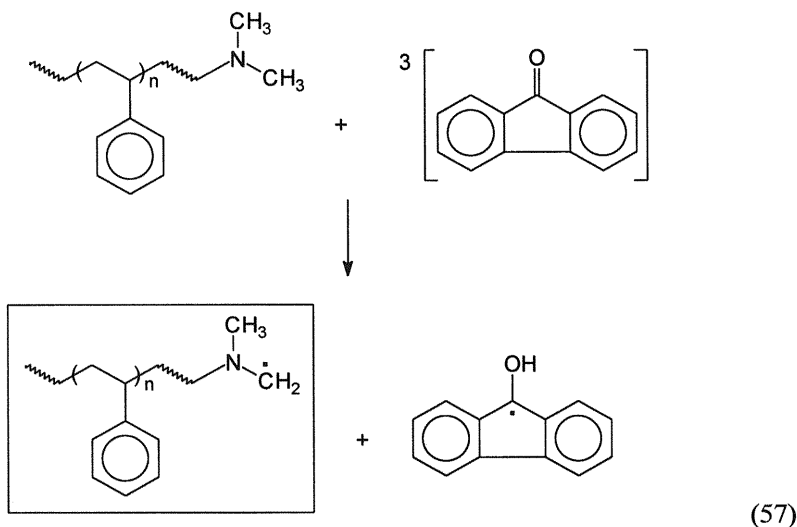
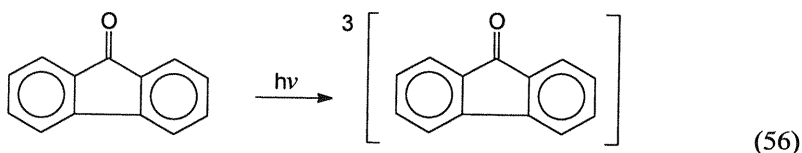
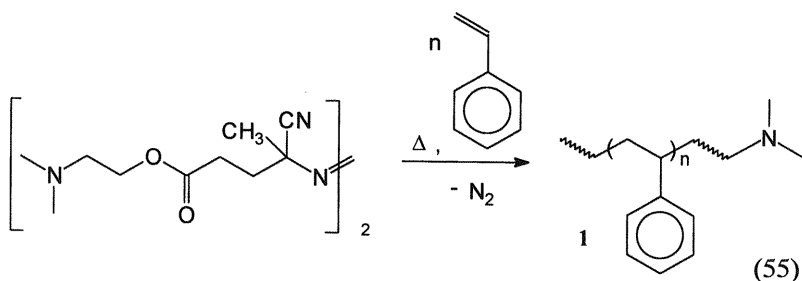
B. Type II Macrophotoinitiators

As has been explained earlier, the mechanism of Type II photoinitiators is based on the phenomenon that triplet states of aromatic ketones readily abstract hydrogen atoms from hydrogen donors, such as tertiary amines. Regarding macrophotoinitiators, there are examples with the ketone and the amine bound to polymer molecules.

Polystyrene terminated with amine functions (**1** in Table 19) has been synthesized using an azo initiator containing terminal amine groups [257]. Heating of this initiator in the presence of styrene yields the desired initiator, because the amine groups are left unaltered by the thermal treatment. In a second reaction step, methyl methacrylate was block copolymerized by making use of the amine sites in a Type II photoinitiating process:

Table 19 Type II Macrophotoinitiators

 <p>1</p> <p>[257]</p>	 <p>2</p> <p>[259]</p>	 <p>3</p> <p>[258, 259]</p>
 <p>4</p> <p>[260]</p>	 <p>5</p> <p>[261]</p>	 <p>6</p> <p>[262, 263]</p>



The macroinitiator **2** (see Table 19) has been obtained by copolymerization of styrene and *N,N'*-diethylamino styrene [258]. The initiator was used for the photopolymerization ($\lambda = 350$ nm) of 2-ethoxyethyl methacrylate with benzoin serving as the coinitiator. This procedure resulted in both homopolymer [poly(2-ethoxyethyl methacrylate, initiated most probably by ketyl radicals)] and the respective graft copolymer. The graft efficiency was pretty high: About 77% of the monomer converted was grafted onto the

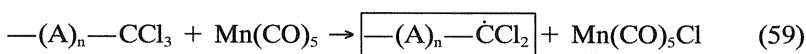
backbone polymer demonstrating the low initiation efficiency of ketyl radicals.

There are various examples of attaching benzophenones to polymers [258–260,264,265]. Containing both benzophenone- and alkylarylcarbonyl-type chromophoric groups, the macroinitiators **4** (Table 19) can be regarded as photoinitiators of Type I and Type II at the same time. They undergo main chain scission upon photolysis, thus producing terminal radicals [260]. The mechanism, although not entirely elucidated, presumably involves the absorption of incident light by the benzophenone residue and a Norrish Type II reaction, leading to chain scission (Type I initiator). Furthermore, a reaction of excited triplet benzophenone sites with the main chain (hydrogen abstraction) has been evidenced (Type II initiator).

The polymer-bound thioxanthone derivatives **5** and **6** (Table 19) have been used in conjunction with amines for free-radical vinyl polymerization. Their initiation efficiency is similar to that of low-molecular-weight analogs.

C. Macrophotoinitiators with Halogen-Containing Groups

When polymers with functional groups like $-CX_3$, $-CHX_2$, or $-CH_2X$ are irradiated ($\lambda = 350\text{--}450\text{ nm}$) in the presence of $Mn_2(CO)_{10}$, terminal carbon-centered macroradicals are formed [280]. Upon absorption of light, $Mn_2(CO)_{10}$ decomposes yielding $Mn(CO)_5$, a compound that reacts with terminal halogen groups according to



These terminal radicals may be used to initiate the polymerization of a second monomer, whereby block copolymers are formed. Notably, homopolymerization is not observed in this process, as no low-molecular-weight radicals are generated upon the reaction of $Mn(CO)_5$ with the macroinitiator.

Naturally, this polymerization procedure may only be applied if the polymer end functionalized with halogen-containing groups is available. There are methods for converting terminal $-OH$, $-NH_2$, and $-COOH$ groups into $-CCl_3$ groups [266]. Furthermore, polymers containing terminal $-CCl_3$ functionalities may be obtained using a bifunctional azo initiator [267].

In addition to being used for block copolymers, the reaction of $Mn_2(CO)_{10}$ with halogen groups attached to polymer backbones has been utilized for the synthesis of graft copolymers [268–273]. A drawback of this method is that in many cases, combination of macroradicals is observed giving rise to cross-linking rather than grafting. Network formation versus

grafting has been studied for a number of trunk polymer–monomer combinations.

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Vinyl Polymerization Initiated by High-Energy Radiation

Ivo Reetz, Yusuf Yagci, and Munmaya K. Mishra

I. INTRODUCTION

The availability of radioactive sources and particle accelerators has stimulated studies on their use for initiating chain polymerizations. These refer mainly to the radiation-induced production of free radicals which are able to initiate vinyl polymerization. First evidence of vinyl polymerization by high-energy radiation was found before World War II [1–3], but it was in the 1950s and 1960s that numerous data on radiation-induced polymerization of many monomers were accumulated. Special attention has also been devoted to the exposure of polymeric substrates to high-energy radiation. The polymer-bound radicals and ions generated under these circumstances in the presence of a monomer may initiate graft copolymerization. Tailor-made polymers with an interesting combination of properties are thus accessible.

High-energy radiation includes electromagnetic x-rays and γ -rays and energy-rich particle rays, such as fast neutrons and α - and β -rays. As far as γ -rays are concerned 1.25-MeV rays emitted by ^{60}Co and 0.66-MeV rays generated by ^{137}Cs have been most frequently used for polymerizations. Electrons (β^- -rays) produced by electron accelerators were also often applied. High-energy electrons (several MeV) were mainly employed for investigating dose-rate effects. Relatively low-energy electrons (0.2–0.5 MeV) are used successfully for industrial curing of various coatings. Electromag-

netic or particle rays other than γ -rays or electrons are seldom used due to several disadvantages such as high cost, lack of penetration, and, in the case of neutrons, residual reactivity.

As far as the absorption of energy by the monomer or polymer is concerned, the predominant effect as γ -rays enter organic substrates is the Compton effect. It involves an electron ejected from an atom after collision. The ejected electron interacts with other atoms to raise their energy level to an excited state. If the electron possesses sufficient energy, another electron is ejected, leaving behind a positive ion. The excited atoms and ions can take part in further reactions in the substrate and transfer their energy or decompose into radicals that give rise to polymer formation in the presence of vinyl monomer:



The cation may then form a radical by dissociation:



The initially ejected electron may be attracted to the cation B^+ forming another radical:



Radicals may also be produced upon a sequence of reactions initiated by the capture of an ejected electron by C:



Another pathway includes the direct homolytic bond rupture upon irradiation with high-energy rays, a process involving the formation of electronically excited C particles:



As described above, the radiolysis of olefinic monomers results in the formation of cations, anions, and free radicals. It is possible for these species to initiate chain polymerizations. Whether radiation-induced polymerization is initiated by radicals, cations, or anions depends on the monomer and the reaction conditions. However, in most radiation-initiated polymerizations, initiating species are radicals [4]. It is usually only at low temperatures that ions are stable enough to react with a monomer [5]. At ambient temperatures

or upon heating, ions are usually not stable and dissociate to yield radicals. Furthermore, the absence of moisture is crucial if one aims at ionic polymerizations [6,7]. Thus, for styrene polymerization at room temperature, polymerization rates are by a factor of 100–1000 times higher for “super-dry” styrene than for “wet” styrene, the difference being due to the contribution of cationic polymerization [8,9]. Radiolytic initiation can also be carried out using additional initiators that are prone to undergo decomposition upon irradiation with high yields.

The reactive intermediates generated when organic matter is exposed to fast electrons generally do not differ much from those obtained by γ -irradiation. The electrons are slowed down by interactions with atoms of the absorber leading to ionizations and excitations. In monomers, ionizations and excitations are produced in a sphere of a radius of ~ 2 –20 nm, a zone referred to as spur.

II. RADICAL POLYMERIZATION

As was shown above, the interaction of high-energy rays with monomers results in the generation of free radicals. In radiation chemistry, the yield of a reaction is generally expressed in terms G values, that is, the number of radiolytically produced or consumed species per 100 eV absorbed. As far as radical vinyl polymerization is concerned, $G(\text{radical})$ values depend on the proneness of a monomer to form radicals. Thus, for styrene, $G(\text{radical})$ values of 0.7 are found; for vinyl acetate, the $G(\text{radical})$ value amounts to ~ 12 (see Table 1).

Table 1 Free Radical Yields $G(\text{Radical})$ Values for a Few Polymerization Mixtures, Bulk and Solution Polymerization

Monomer	Solvent	$G(\text{radical})$
Styrene	None (bulk)	0.69
	Benzene	0.76
	Toluene	1.15
	Chlorobenzene	8.0
	Ethyl bromide	11.8
Methyl methacrylate	None (bulk)	11.5
	Methyl acetate	10.9
Vinyl acetate	None (bulk)	12.0
	Ethyl acetate	12.0

Source: Ref. 10.

Radiation-induced polymerizations may be performed in bulk, in solution, or even as emulsion polymerization [11,12]. For solution polymerization, the possibility of generating radicals stemming from solvent has also to be taken into account. Notably, in contrast to photopolymerization, where solvents transparent to incident light are used, usually high-energy radiation is absorbed by all components of the polymerization mixture, including solvent. As is seen in Table 1, for a monomer with a low $G(\text{radical})$ value, the overall radical yield and, therefore, the polymerization rate may be enhanced by using solvents that easily produce radicals (e.g., halogen-containing solvents).

In some cases of solution polymerization, there is efficient energy transfer from excited solvent molecules to monomer molecules or vice versa [13,14]. For example, in the case of styrene polymerization in *n*-dibutyl disulfide (DBD), an energy transfer from styrene to DBD has been observed [15]. Very strong sensitization occurs in mixtures containing carbon tetrachloride. By the addition of $\sim 3\%$ of this substance, the polymerization rate of styrene rises by a factor of 3 [16]. The acceleration of styrene polymerization by addition of small amount of methanol has also been reported [17]. This effect has been explained in terms of a reaction of protons, stemming from methanol, with radiolytically formed styrene-based anion radicals, transforming the latter into initiating radicals. Furthermore, higher polymerization rates may be brought about by small concentrations of typical radical initiators, such as hydrogen peroxide [18,19], that readily generate radicals upon irradiation.

III. GRAFTING AND CURING

Radiolytical grafting is an often performed method for the production of specialty polymers with interesting surface and bulk properties. Important areas for radiation-induced grafting onto solid polymers include the development and production of hydrophilic surfaces and membranes, which find application in separation technology and in medicine [20–29]. Radiation is used to activate the base polymer, onto which the monomer present is grafted. Radicals and/or ions produced adjacent to the polymer backbone act as initiating sites for free-radical or ionic polymerization. The striking advantage of this method is its universality. In fact, virtually all polymers may be activated for grafting by high-energy radiation to an extent that compares well with chemical initiation. Furthermore, there is no requirement for heating the backbone trunk what would be the case if thermal activation was applied.

Upon exposing a polymer to high-energy radiation, radiolytically induced chain scission or cross-linking has also to be taken into account [30]. If the irradiation takes place in the presence of oxygen, chain scission is often observed. Oxygen acts as a radical scavenger and forms reactive peroxides when reacting with the polymer-bound radicals, giving rise to degradation processes referred to as autoxidation.

Three experimental approaches of radiolytical grafting have to be distinguished.

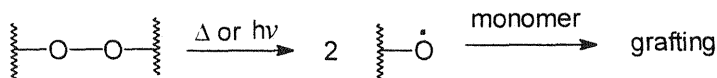
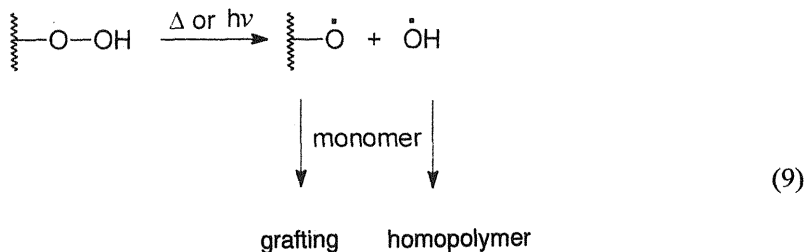
1. The *preirradiation technique* consists of two distinct steps: irradiation of the backbone polymer *in vacuo* or an inert gas in the absence of monomer and, subsequently, addition of a monomer. Obviously, sufficient lifetimes of the reactive species and also high reactivities toward the monomer is necessary. For trapped radicals, this generally requires some degree of crystallinity or a glassy state in the polymer and storage at low temperatures [20,31].

In the second, the actual grafting step, the monomer has to diffuse to the active centers of the polymer. In some applications, heating is applied for increasing the mobility of both the monomer and irradiated polymer. However, a disadvantage of heating in this step is that recombination of polymer-bound radicals become more likely, owing to the high overall particle mobility. Solvents or swelling agents also lead to a faster diffusion of monomer to the reactive site of the backbone trunk.

2. In many cases, higher grafting yields are obtained when the preirradiation is performed in oxygen or in air [32,33]. This phenomenon, which is ascribed to the formation of peroxides at the base polymer, is utilized for the so-called *peroxide technique* [32–36]. Oxygen present during irradiation reacts with the reactive polymer-bound radicals generated upon irradiation. In a second step, the polymeric hydroperoxides are decomposed upon heating or ultraviolet (UV) irradiation in the presence of a monomer. The oxygen-centered, polymer-bound radicals generated give rise to a graft copolymer. Not being attached to the backbone trunk, hydroxyl radicals initiate homopolymerization of the monomer present:



If peroxy radicals react together, peroxides are produced, which yield only polymer-bound radicals upon irradiation. Therefore, homopolymer formation does not take place. However, these peroxides are harder to activate than hydroperoxides:



Another possibility of preventing homopolymer formation is the addition of reducing agents, such as the Fe^{2+} containing Mohr's salt [22–24,33,36], to the monomer.

As was pointed out above, peroxides are also precursors of autoxidation. In order to avoid excessive degradation of the trunk polymer, control of irradiation doses is necessary.

3. The simultaneous irradiation of a monomer and a base polymer is referred to as *mutual radiation grafting technique*. In this method, the monomer may be present as vapor, liquid, or in solution. In order to avoid degradation, the polymerization mixtures are mostly freed from oxygen.

Following this technique, reactive sites are produced on both the backbone trunk and the monomer, the latter giving rise to a sometimes appreciable yield of undesired homopolymer. In fact, the radical formation yield of the trunk polymer has to be high in comparison with that of the monomer in order to have little homopolymer formation. Trunk polymers that are very suitable in this respect are poly(vinyl chloride) (abstraction of Cl), wool, cellulose [37], poly(amides) [38–68], or aliphatic-type polymers, such as poly(ethylene) (facile C—H bond scission) [69]. Polymers with aromatic rings in the backbone are unsuitable because they are generally quite radiation resistant. The efficiency of grafting is usually high because the reactive species produced react immediately with monomer. Another advantage is that relatively low radiation doses are sufficient for grafting, which is particularly important for radiation-sensitive base polymers, such as poly(vinyl chloride). In many cases, radiation protection by the monomer may be observed. Vinyl compounds often protect aliphatic substances from undergoing radiolytically induced reactions, a phenomenon ascribed to scavenging reactions, particularly involving hydrogen atoms [70,71].

The presence of solvents or swelling agents exerts a significant influence on the copolymerization and sometimes on the properties of the co-

polymer [72–79]. For example, if styrene is grafted onto cellulose in the presence of *n*-butanol as a swelling agent, grafting is observed only at the surface of the cellulose sample. On the other hand, if methanol is used instead of butanol, grafting occurs at the surface as well as in the cellulose bulk [80]. For many backbone polymers, the yield of grafting may be significantly improved by using accelerating additives such as mineral acids [81–84]. Furthermore, higher grafting rates may be obtained by means of thermal radical initiators, such as 2,2'-azobisisobutyronitrile [85].

A wide variety of trunk polymers have been used for grafting reactions [13]. As an example, grafting onto nylon was of interest because by grafting, surface and certain bulk properties of this important synthetic fiber may be modified. Using γ -rays for activation, various vinyl monomers were grafted onto nylon-6 backbone. The grafting of acrylic acid [86–89] on nylon was carried out using a ^{60}Co source at room temperature. The amount of acrylic acid grafted on the fiber increased linearly with monomer concentration [89]. The radiation-induced graft copolymerization of styrene, acrylonitrile [38–53], methyl methacrylate [54–56], methacrylic acid [57–59], and acrylamide [60–64] and its derivatives, such as *N*-methylol acrylamide [60,65–68] onto nylon-6 was studied by various workers using a ^{60}Co source. The kinetics of the process was studied by measuring radical destruction rates and the weight increase. Usually, no homopolymer was obtained [44]. The graft copolymer is evenly distributed in the amorphous area of the fiber. The fiber's crystallinity remained unchanged [51].

Sumitomo and Hachihama [32,90], Skyes et al. [60], Okamura et al. [91], and Armstrong et al. [92–94] compared various procedures of grafting and concluded that preirradiation of nylon in air followed by heating it in monomer (ethyl acrylate) at 60–100°C yielded higher grafting yields than those obtained by mutual irradiation technique or by preirradiation *in vacuo*.

A commercially important technique that is in some respect similar to radiolytically induced grafting is the *curing* of coatings by high-energy rays [95]. For curing, preformed polymers, oligomers, or sometimes monomers are irradiated mainly by means of electron beam machines, whereby reactive sites, mainly radicals, are generated. The radicals are adjacent to the polymer backbone and react together, leading to cross-linking in the irradiated part of the coating. As prepolymers, mostly acrylate-based polymers prepared by monomer polymerization or the acrylation of a backbone polymer such as a poly(urethane), poly(ester), poly(ether), or epoxy polymers with relatively low molecular weight (≈ 3000) are used [96–99]. Recent studies suggest that upon curing at room temperature, also, ions are produced that have to be taken into account for explaining the curing mechanism [100,101].

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9

Functionalization of Polymers

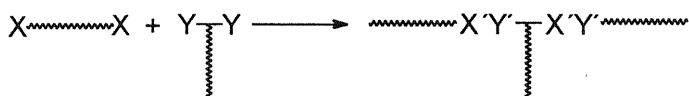
Yusuf Yagci and Munmaya K. Mishra

I. INTRODUCTION

Design and synthesis of materials with novel properties is becoming an interestingly important aspect of polymer chemistry [1,2]. Quite often, desired properties are not attainable by the properties of a single homopolymer. The synthesis of block structures is one way to adjust properties of polymers. Blocking reactions are generally accomplished in two ways: (i) successive addition of appropriate monomers in living polymerization [3] which allows preparation of block copolymers containing two or more different segments and (ii) polymers with functional end groups (telechelics) can be converted to initiating species by external stimulation such as heat, light, or chemical reaction [4,5]. Alternatively, these polymers, based on the reaction of the functional groups with other suitable low-molar-mass compounds or polymers, can be used in block condensation (Scheme 1). In the latter case, the number and the location of the functional group are quite important for the overall structure of the block condensate. Polymers must possess exactly two functional end groups to yield polycondensates with high molecular weight. Functional end groups located at the end of one chain can undergo similar condensation reactions. In this case, graft copolymers are formed (Scheme 2). In addition to their use in block and graft copolymerizations,



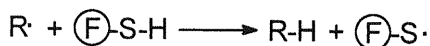
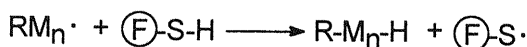
Scheme 1



Scheme 2

end groups have various effects on the properties of the incorporated polymer such as dyeability and hydrolytic and thermal stability.

Functionalization of polymers is usually achieved by either anionic [3] and cationic [4] polymerization mechanisms in which chain-breaking reactions are of minor importance. On the other hand, radical vinyl polymerization, although easy to handle and can be applied to the most vinyl monomers, lack the following disadvantages. Noninstantaneous initiation and the random nature of the termination yield polymers much higher polydispersities than those obtained by ionic processes. In order to have true telechelics (i.e., each polymer possesses two functional groups), termination should occur exclusively by combination. This requirement is not fulfilled by many monomers. Whereas styrene and its derivatives, and acrylates terminate mainly by combination, methacrylates undergo disproportionation. The latter would result with monofunctional polymers. Providing one type of primary radicals is formed (i.e., primary radicals do not participate in hydrogen abstraction reactions), this problem may be overcome by working at higher initiator concentrations. Chain transfer reactions were also frequently used to functionalize polymers. With the system consisting of a functional chain transfer agent, the chain transfer agent reacts not only with the propagating radical but also with the primary radicals derived from the initiator (Scheme 3). Although it can be reduced to very low levels, nonfunctional groups are also formed.



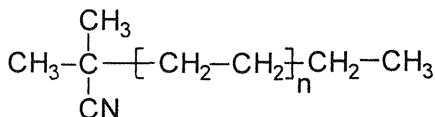
Scheme 3

II. FUNCTIONALIZATION TECHNIQUES

B. Initiator Techniques

1. Azo Initiators

Azo initiators are, by far, the most widely employed initiators for polymer functionalization. The well-known azo initiator 2,2'-azobisisobutyronitrile (AIBN) is highly efficient to introduce cyano end groups to polymers. Ethylene [6] and styrene [7] were polymerized and AIBN to yield the corresponding polymers with the functionalization values of 1.7 and 2, respectively. High functionalization in the case of polystyrene was due to the primary radical combination as was confirmed by nuclear magnetic resonance (NMR) studies [8,9]. Gas chromatography–mass spectroscopy (GC-MS) studies reviewed that the relatively lower functionalization in the case of polyethylene results in part from the occurrence of some termination by disproportionation. The following product stemming from disproportionation was identified (Scheme 4).



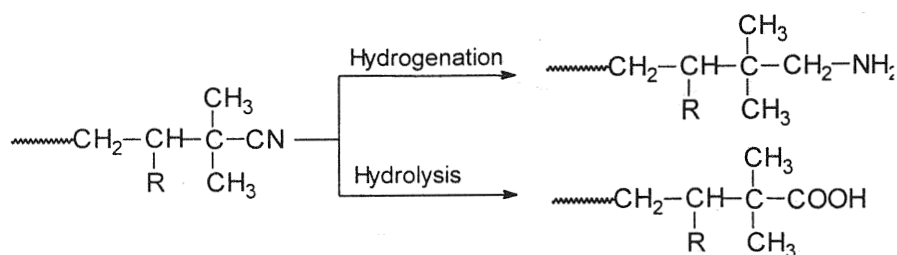
Scheme 4

Primary amine- and carboxy-terminated polymers may be obtained [7] from AIBN-initiated telechelics by subsequent hydrogenation and hydrolysis, respectively (Scheme 5).

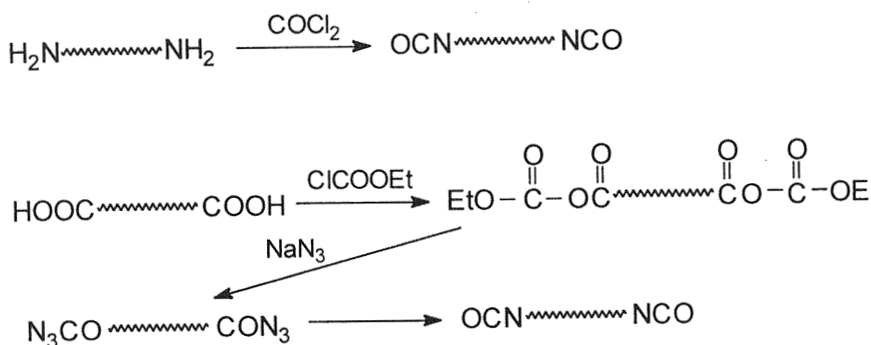
Isocyanate functional groups can be introduced [7] by two methods as illustrated in Scheme 6. The former method, which requires less reaction steps, appears to be more suitable. In order to obtain polymers with NH_2 terminal groups, an alternative method was developed [10]. An azo initiator containing (acyloxy)imino groups were heated in the presence of styrene. Irradiation of the resulting polymers, in the presence of a benzophenone sensitizer and subsequent hydrolysis, yielded polymers with primary amino groups (Scheme 7). Successful functionalization was approved by polyamidation with bifunctional acid chlorides. Regarding photoactive group functionalization, the azo initiators listed in Table 1 have been successfully applied in free-radical polymerization.

Crown ether moieties, capable of binding certain ions, have also been introduced on polymers by using the functional initiator approach [18,19].

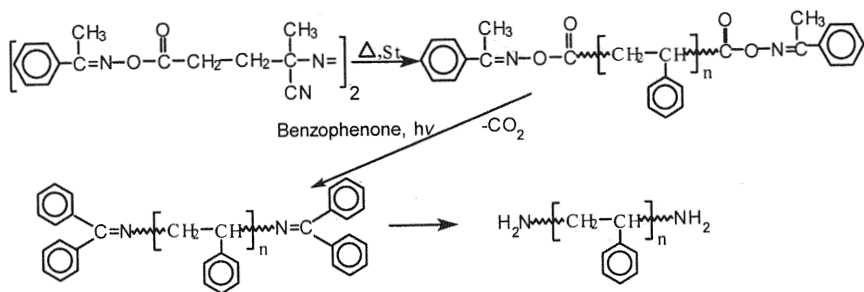
A variety of other functional initiators have been synthesized by modifying AIBN's methyl [20] or nitrile [21] groups. Azo compounds containing hydroxyl, carboxyl, carboxyl chloride, and isocyanate groups are the most frequently used initiators for the functionalization of polymers from a wide



Scheme 5



Scheme 6

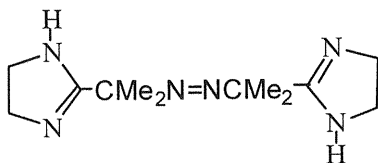


Scheme 7

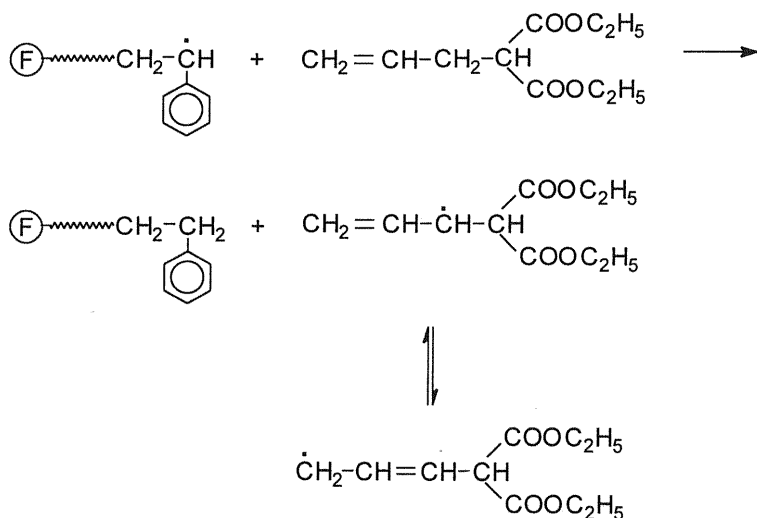
Table 1 Azoinitiators (I)^a Used for Photoactive Group Functionalization and Applications

Azoinitiator (R=)	End Group	Application	References
	Amino	Polyamidation	10
	N-Acyl dibenzazepine	Chain extension, block copolymerization	11
	Benzoin	Block copolymerization	12-15
	Dimethyl amino	Block copolymerization	16
	Trichloroacetyl	Block copolymerization	17
$^a I = \left[\text{RO}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2-\text{CH}_2-\underset{\text{CN}}{\overset{\text{CH}_3}{\text{C}}}-\text{N} \right]_2$			

range of monomers [22–26]. Polydienes possessing these groups are of particular interest because they find application as polymeric binders [27] and to modify properties of polyamides and polyesters by introducing soft segments. Polybutadiene [28] with CN or COOMe groups, and polyisoprene and polychloroprene [29–31] with OH or COOH groups have been successfully prepared via the functional initiator approach. Hydroxy-terminated polyacrylonitrile [24] and poly(acrylonitrile-*co*-styrene) [32] were also prepared. Polystyrenes with monofunctional α -imidazole groups were synthesized by using the azo initiator with the following structure (Scheme 8):

**Scheme 8**

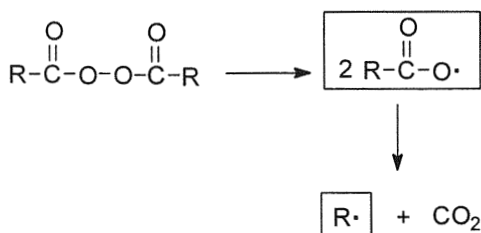
As stated in section I, the termination mode of the particular monomer determines the number of functionalities per macromolecular chain. Most monomers undergo both unimolecular and bimolecular termination reactions. It is often observed that both respective monofunctional and bifunctional polymers are formed and well-defined functional polymers cannot be prepared. The use of allylmalonic acid diethylester in free-radical polymerization has been proposed to overcome the problems associated with the aforementioned functionality. In the presence of the allyl compound, the free-radical polymerization of monomers, regardless of their termination mode, proceeds entirely with the unimolecular termination mechanism, as shown in Scheme 9. Because allyl compounds lead to degradative chain transfer, the resulting allyl radical is quite stable due to the allyl resonance. Monofunctional polystyrene, polyvinylacetate, and poly(*t*-butyl methacrylate) were prepared by using this approach [33]. Subsequently, various macromonomers were derived from these polymers.



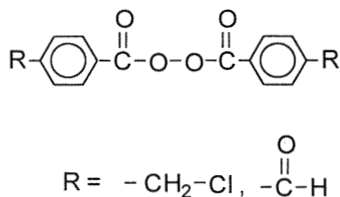
Scheme 9

2. Peroxides

Acylperoxides are less frequently used in polymer functionalization due to the fact that upon heating, two different type of radicals are formed (Scheme 10):

**Scheme 10**

On the other hand, aryloxy peroxides [34], although less reactive, have led to polystyrene telechelics. For example, benzyl chloride- and benzaldehyde-terminated polymers were obtained directly from the following benzoyl peroxides without further purification (Scheme 11):

**Scheme 11**

Dialkylperoxycarbonate initiators were used for ester functionalization. Monomers such as ethylene [35], methyl methacrylate [36], and styrene [37] were reported to be polymerized by these initiators. The terminal ester groups can easily be transformed into hydroxyl groups by hydrolysis [27].

Redox reactions involving peroxides are another efficient way to prepare telechelics. Hydroxyl-terminated polydienes [37] and carboxylic acid-terminated polytetrafluoroethylenes [38] were synthesized by using H_2O_2 and potassium peroxy disulfate, respectively, via redox reactions.

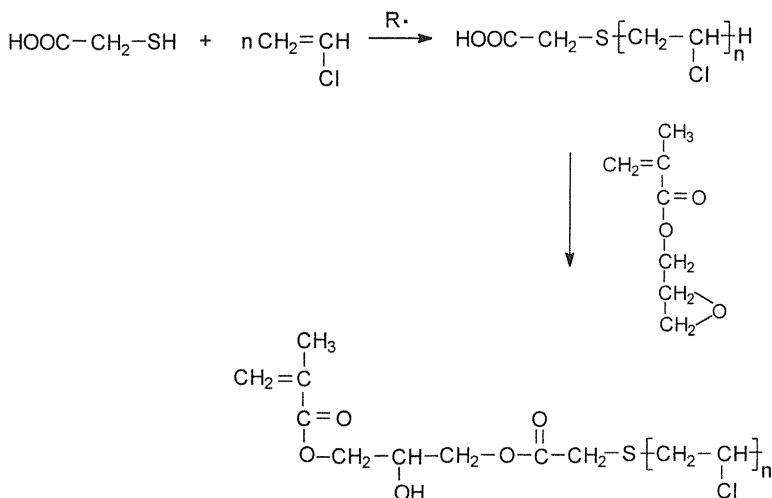
B. Transfer Reactions

1. Transfer Agents

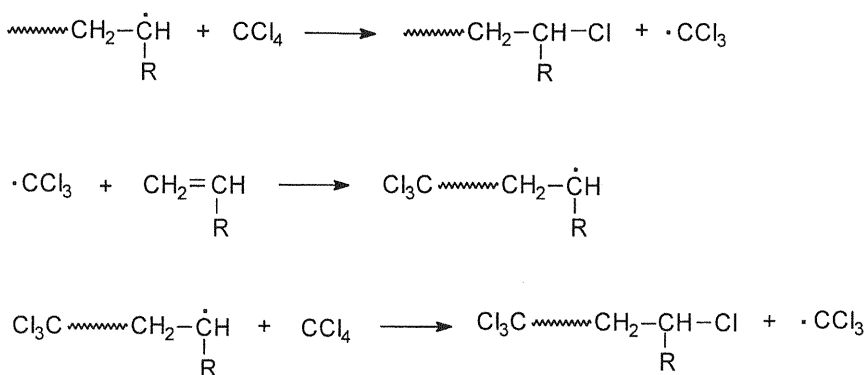
In addition to the initiator-controlled polymer functionalization, transfer reactions may result in functional polymers. In free-radical polymerization, thiols are often employed as chain transfer agents. Chain transfer reactions involving thiols proceed via atom abstraction, as illustrated in Scheme 3. Consequently, these molecules do not offer any scope for introducing functionalities at both ends. However, monofunctional telechelics have been successfully prepared by using thiols. For example, Boutevin and co-workers [39,40] introduced polymerizable vinyl groups to polyvinylchloride accord-

ing to that strategy. 3-Mercaptopropionic acid has been used as a functional chain transfer agent, and the carboxylic acid group has then been reacted with glycidyl methacrylate.

Polystyrene macromonomers [41] with molecular weights of 10^3 – 10^4 were also prepared. Similar experiments [42,43] using 2-mercaptoethanol, and subsequent treatment of the resulting polymer with methacryloyl chloride led to methacryl end-capped polymethacrylates and polyvinylchloride. Typical reactions in the case of polyvinylchloride are illustrated in Scheme 12.



Scheme 12



Scheme 13

Free-radical polymerization in the presence of a chain transfer agent (telogen) is often called a telomerization reaction. Many different telogens

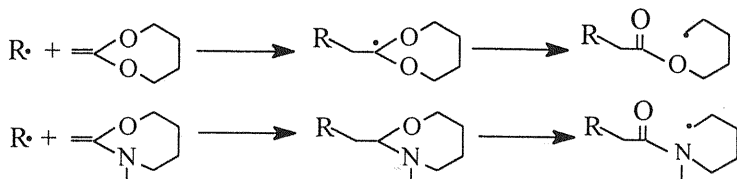
have been reported [44]. The most studied and well-documented telogen is CCl_4 . Other analogous halogen compounds, namely CBr_4 and CHI_3 , are not suitable due to their very high transfer constants which yield only oligomeric materials. General reactions involving telomerization are represented for the case of CCl_4 in Scheme 13.

2. Iniferters

Disulfides are useful compounds in free-radical polymerization of vinyl compounds. The S—S bond present in the molecule readily decomposes to form thiyl radicals, which act as both initiators and terminators. The disulfides are also used as chain transfer agents. These compounds are called iniferters by anomie to their roles in initiation, transfer, and termination reactions. Polymers prepared with disulfides possess terminal weak and easily dissociable carbon–sulfur bonds which allow further addition of monomer on a terminated polymer. When the functional group is incorporated to the disulfides, the obvious benefit would be the possibility of the preparation of functional polymers. For example, carboxylic acid and amino functionalities were introduced to polystyrene using the corresponding disulfides [45]. Diamino functional poly(*t*-butyl acrylate) was also prepared [46]. In this case, polymers were readily hydrolyzed to polyacrylic acid possessing amino terminal groups which is a useful material for the application of polyelectrolytes. The iniferter properties of the tetraalkyl thiuram disulfides during free-radical vinyl polymerization were also exploited to end functionalize poly(methyl methacrylate) and polystyrene [47,48].

3. Addition–Fragmentation Reactions

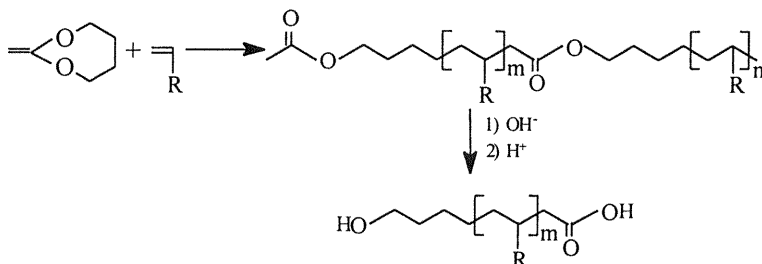
Free-Radical Copolymerization of Vinyl Compounds with Unsaturated Heterocyclic Monomers. Free-radical ring-opening polymerization of cyclic ketenacetals and their nitrogen analogous occurs via formation of carbonyl bond at the expense of a less stable carbon–carbon double bond as depicted in Scheme 14 [49–56]:



Scheme 14

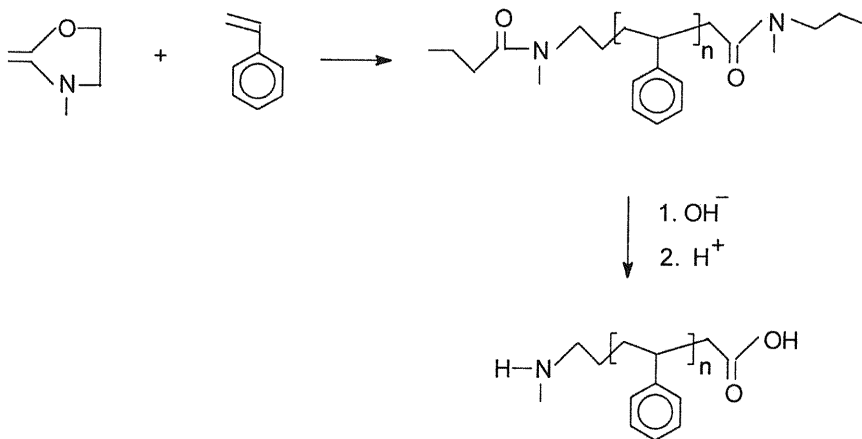
Functional polystyrene and polyethylene possessing hydroxy and carboxylic end groups in the same molecule were prepared by taking advantage

of this type of so-called addition fragmentation reaction. For this purpose, 2-methylene-1,3-dioxepane was polymerized with excess styrene and ethylene. Hydrolysis of the resulting polymers yielded desired telechelics (Scheme 15):



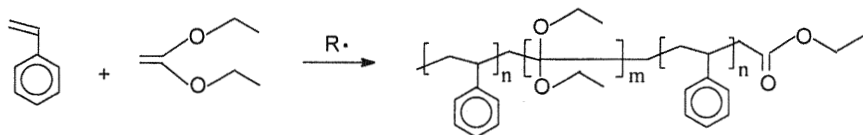
Scheme 15

Similar reactions of the nitrogen derivative gave polystyrene with an aminomethyl group at one end and a carboxy group at the other end of the molecule (Scheme 16):



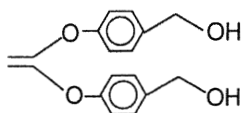
Scheme 16

Open-Chain Ketenacetals. Open-chain ketenacetals undergo addition–fragmentation reactions as the cyclic ketenacetals to form an ester bond [56]. These molecules do not yield high-molecular-weight homopolymers due to the degradative chain transfer reaction. The radical copolymerization of equimolar amounts of styrene and diethyl ketenacetal, however, gives oligomeric products possessing ethoxy carbonyl groups at the chain end (Scheme 17):



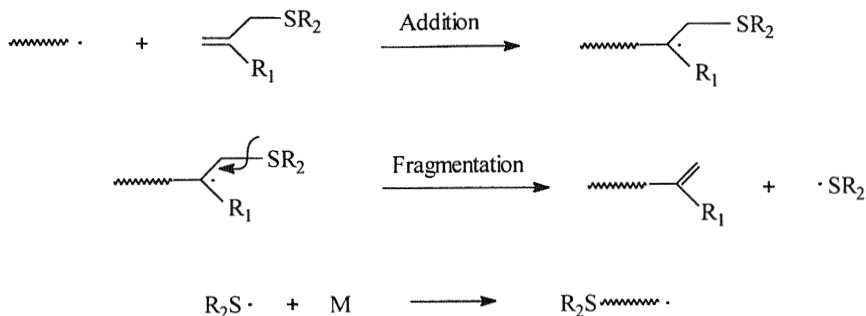
Scheme 17

In this case, diethyl ketenacetal acts as both monomer and moderately effective chain transfer agent. Introduction of a phenyl group increased the extent of cleavage and the efficiency of the chain transfer reaction. Thus, benzyl and ester functional polymers are essentially obtained. Ketenacetal that possesses benzylalcohol groups (Scheme 18) is able to yield polymers with two hydroxy groups at the chain ends [56].



Scheme 18

Allylic Sulfides. Among many other compounds which undergo addition–fragmentation reactions, appropriately substituted allylic sulfides have been shown to be efficient transfer agents in free-radical polymerization [57–59]. The average chain transfer constants of these compounds are in the range 0.3–3.9. Thus, molecular weight can be controlled by efficient transfer reactions. These molecules can be used to prepare a wide range of macromonomers and monofunctional and bifunctional polymers when functionality is introduced into one or both of the substituents R_1 and R_2 (Scheme 19):

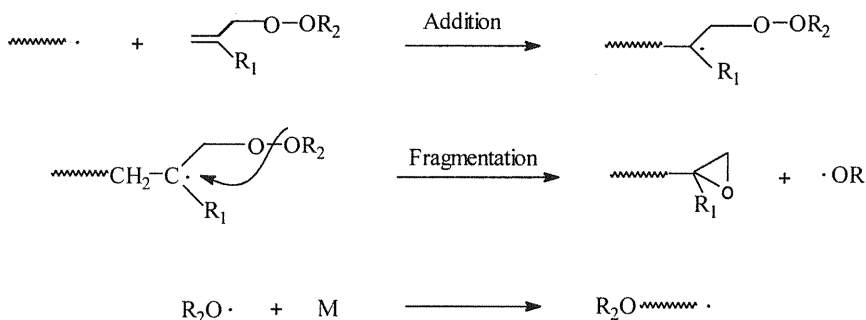


Scheme 19

Other allylic compounds which participate in addition–fragmentation reactions analogous to allylic sulfides include allylic bromides, allylic phos-

phanate, and allylic stannane [60,61]. The high chain transfer constants indicate that these compounds can also be used to prepare functional polymers.

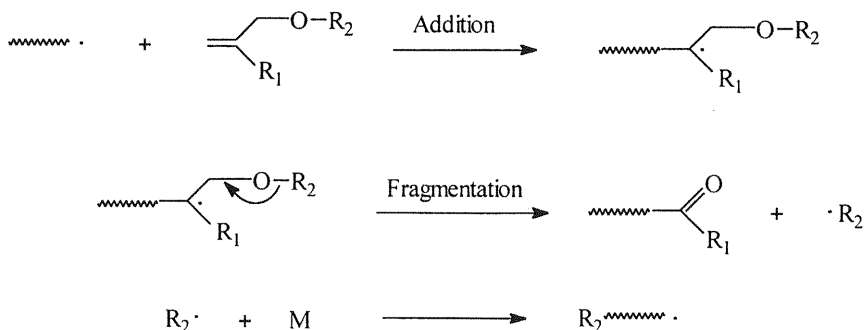
Allylic Peroxides. Allylic peroxides are another class of compounds which undergo addition–fragmentation reactions [62,63]. The striking advantage of allylic peroxides derives from the fact that epoxy functional polymers can be prepared by the addition of propagating radical to the double bond followed by γ -scission according to the following reactions (Scheme 20):



Scheme 20

Epoxy functionalization of polystyrene via the above mechanism was evidenced by ^1H -NMR and ^{13}C -NMR analysis of the resulting polymer.

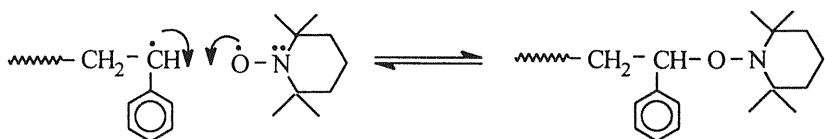
Vinyl Ethers. Chain transfer reactions involving suitably constituted vinyl ethers [64,65] also proceeded via addition–fragmentation reactions, as illustrated in Scheme 21. Benzyl and benzoyl groups were thus incorporated into polystyrene and poly(methyl methacrylate).



Scheme 21

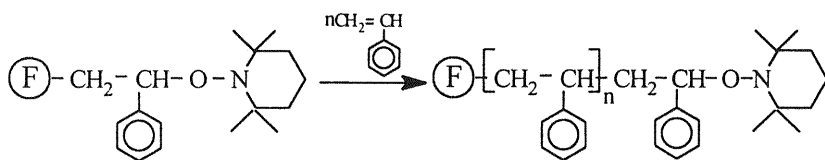
C. Living Radical Polymerization

As described in Chapter 10, the use of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) and its derivatives for the bulk polymerization of certain vinyl monomers, such as styrene, results in a “living” process according to the following reaction [66–70] (Scheme 22):

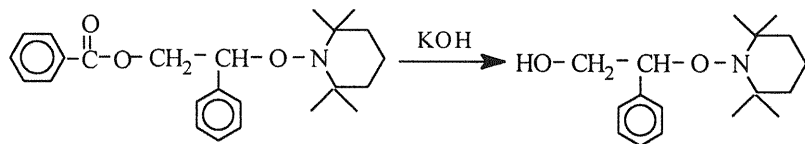


Scheme 22

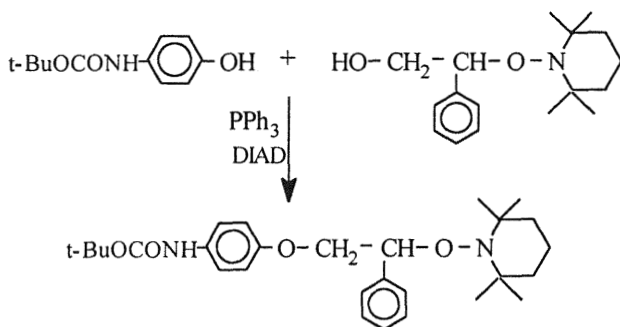
The stable radical-mediated polymerization represents a promising approach to defined homopolymers and block copolymers. Recently, Hawker and Hedrick [71] demonstrated the potential use of the living radical polymerization for the preparation of functional polymers. Two strategies were followed. The first method involves the synthesis of functionalized monoadducts of styrene and TEMPO and their use in styrene polymerization (Scheme 23). The hydroxy functionalized initiators were prepared by hydrolyzing the ester functionality of the adduct (Scheme 24). Protected amino groups were also introduced by further modification of the latter. Hydroxy groups were treated with *N*(*tert*-butoxycarbonyl)-4-aminophenol, as illustrated in Scheme 25.



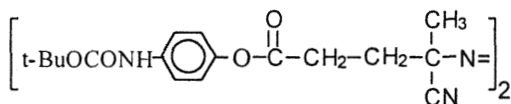
Scheme 23



Scheme 24



Scheme 25



Scheme 26

Polymerization of styrene with these initiators gave hydroxy and protected amino-terminated polymers with narrow polydispersities (i.e., M_w/M_n : 1.1–1.6). The t -Boc amino group in the latter case can be deprotected by trifluoroacetic acid to eventually yield monofunctional amino-terminated polystyrene. An alternative procedure is based on the use of a functional initiator possessing the desired groups (Scheme 26) together with TEMPO.

Both methods were successfully applied to functionalize one chain end with diamino groups. The utility of monofunctional and bifunctional polymers in the preparation of block and graft copolymers was also demonstrated by using a dianhydride and a diamine as comonomers in a manner similar to that described in Section I. No homopolystyrene was detected, indicating the accurate functionalization of the chain end by living radical polymerization.

III. CONCLUSION

Free-radical polymerization is still the most important process in view of its wide utility and due to the various synthetic possibilities described in this chapter. It has considerable potential for polymer functionalization.

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Living Radical Polymerization

Yusuf Yagci and Munmaya K. Mishra

I. INTRODUCTION

Radical polymerization is a very useful method for a large-scale preparation of various vinyl monomers, which has a number of merits arising from the characteristics of the intermediate free radicals. In recent years, however, interest has been directed toward polymers with specific properties. The importance of the synthesis of polymers with controlled molecular architecture has been augmented due to the rising demands for the specialty polymers. Living polymerization is an essential technique for synthesizing polymers with controlled structure (i.e., polymers with controlled molecular weight and narrow molecular-weight distributions). Moreover, living polymerization techniques allow preparation of macromonomers, macroinitiators, functional polymers, block and graft copolymers, and star polymers. In this way, the need for specialty polymers having a desired combination of physical properties can be fulfilled. Control of such complex architectures by living polymerization has largely been achieved using living anionic or cationic and group transfer polymerization techniques. From the practical point of view, however, these techniques are less attractive than free-radical polymerization, because the latter can be performed much more easily. Moreover, ionic techniques are limited to a few vinyl monomers, whereas prac-

tically all vinyl monomers can be homopolymerized and copolymerized by a free-radical mechanism.

A long-lasting goal has been the development of practical living radical polymerization methods. In general, radical polymerization suffers from some defects (i.e., the control of the reactivity of the polymerizing monomers and, in turn, the control of the structure of the resultant polymer). In ionic living systems, the chain ends do not react with one another due to the electrostatic repulsion. On the other hand, the growing radicals very easily react with each other via combination and/or disproportionation. Therefore, it has long been considered that the synthesis of polymers with a controlled structure by radical polymerization in a homogeneous system is almost impossible. Following the living anionic polymerization of alkenes and dienes [1–3], many attempts have been made to find a living radical polymerization to solve some of the problems associated with the conventional radical polymerization systems. Despite considerable progress, a truly living radical polymerization has not been developed. Several new living polymerization systems which were previously difficult to control have been developed during the past years. Higashimura et al. established that polymerization of alkyl vinyl ethers using HI/I_2 or ZnI_2 proceeds via a living mechanism [4]. Another recent advance has been the development of the living carbocationic polymerization of isobutylene by Mishra and Osman [5,6] and Kennedy et al. [7–9]. This may be a reason why living radical polymerization has recently attracted a revitalized worldwide interest. The strategies used to improve the “livingness” of the cationic systems may be used successfully in radical systems. This chapter presents the earlier approaches to living systems and the recent developments. At the end of this section, credit must be given to former review work regarding living radical polymerization [10–13]. Most of these publications primarily concern the iniferter method.

II. INITIATING SYSTEMS

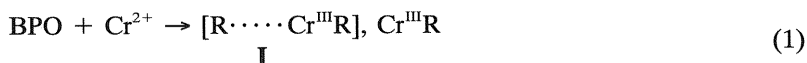
A. Chromium Ion/Benzoyl Peroxide System

The radical living polymerization of vinyl monomers such as methyl methacrylate (MMA) in *N,N'*-dimethyl formamide (DMF) at 30°C or below was demonstrated by Lee et al. [14] using an aged Cr^{2+} plus benzoyl peroxide (BPO) initiating system. The polymerizations were carried out by adding monomer to the aged mixture of Cr^{2+} in BPO in DMF (aging process at 10°C, Cr^{2+} changing completely to Cr^{3+}). Reportedly, the degree of polymerization (DP) of the polymer increased with monomer conversion and the

unimodal gel permeation chromatography (GPC) elluogram of poly(methyl methacrylate) (PMMA) shifted with conversion.

The polymerization mechanism involving the complexed radicals on chromium (III) was proposed as follows. The reaction of Cr^{2+} with BPO by the aging process produces the long-lived complexed radical I and ordinary Cr^{III} .

1. Initiation



where $\text{R} = \text{C}_6\text{H}_5\text{CO}_2$

2. Propagation

When monomers (M) are added, I initiates the polymerization, yielding the complexed polymer radical II:



where $\text{P} \cdot$ is the polymer radical.

In this way, the transition metal complex (Cr^{3+}) stabilizes the growing radical. In other words, the polymerization is based on the reaction of growing radicals with the complex to reversibly form persistent radicals. DP increases with monomer conversion because the complexed radical is screened by Cr^{III} , and the following bimolecular terminations are prevented:



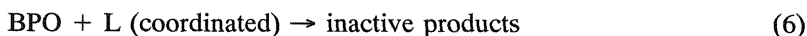
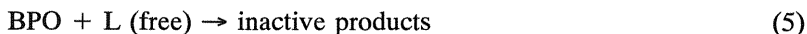
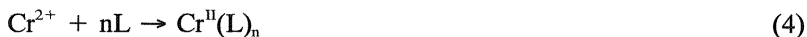
The effect of solvents on the polymerization of MMA with this initiator was studied [15] in electron-donating solvents hexamethylphosphorictriamide (HMPA) + DMF, DMF, and dimethylsulfoxide (DMSO) + DMF. The initial rate of polymerization in the mixed solvent (HMPA + DMF) is approximately three times that of DMF. The linear plots of conversion against time and the plots of the number-average degree of polymerization (DP) versus conversion pass through the origin which is in favor the living po-

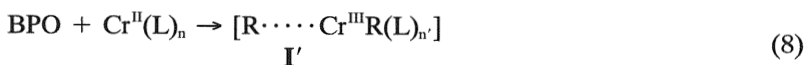
lymerization. The rate constants of the propagation step are very small compared with those for a conventional free-radical polymerization. The rate of polymerization at 30°C decreases with time during prolonged polymerization. There is a steep increase of DP in the region of high monomer conversion. The molecular-weight-distribution curves of polymer obtained at 20°C have single peak shifts with conversion, but these curves become bimodal at high conversion. Typical dead-end polymerization occurs at 50–60°C; that is, the polymerization stops before reaching about 10% conversion. The DP values of polymer obtained at high temperature are relatively larger than those obtained at a low temperature, and increase with polymerization time even after polymerization has stopped. This was explained in terms of recombination of growing radicals (i.e., the polymer radicals complexed with Cr^{III}), which are the propagating species in the living polymerization.

The “living” radical polymerization of MMA with the aged Cr^{2+} plus BPO system in the presence of various amines [16] as the ligand has also been studied in DMF. Aliphatic amines such as ethylenediamine diminished the rate of polymerization, whereas dipyrldyl (dipy) and *o*-phenanthroline (phen) accelerated the polymerization rate as follows: phen > dipy > pyridine = none. Specifically, the rate of polymerization in the presence of phen had a maximum value at $[\text{phen}]/[\text{Cr}^{2+}] = 0.5$.

The retardation of polymerization by aliphatic amines was explained by the interaction of BPO with free and coordinated amines. The order of addition of amines to the initiating system has also a marked effect on the rate of polymerization. Two procedures were undertaken for the addition of ligand (L). In the first procedure, three components (i.e., BPO, Cr^{2+} , and L) are reacted at the same time (i.e., $[\text{BPO} + \text{Cr}^{2+} + \text{L}]$). In the second procedure, BPO was added to the aging of Cr^{2+} and L (i.e., $[\text{BPO} + (\text{Cr}^{2+} + \text{L})]$). The addition of amine by the first procedure retarded the rate of polymerization, whereas the addition of amine by the second procedure accelerated the rate up to a maximum value.

It was found that the additions of these amines and *n*-butylamine inhibited the conventional free-radical polymerization initiated by BPO in DMF. This indicates that these amines act as deactivators for the initiation of free-radical polymerization by BPO. From these results, the following reactions for the aging step were proposed:





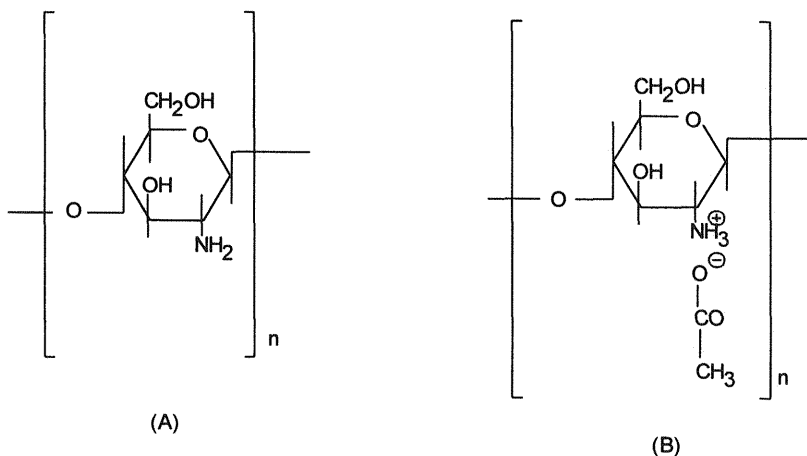
Under the first procedure, reactions (4)–(8) may occur competitively. When the contribution of reaction (5) or (6) is relatively large, the rate of polymerization diminishes because the consumption of BPO lowers the formation of initiating species [17]. The diminution of R_p with the increase of amine concentration indicates that the contribution of reactions (5) and (6) is enhanced with the increase of amine concentration. The chromium ion/BPO initiating system has very low reactivity toward certain monomers, namely styrene, vinyl acetate, and vinyl chloride [15].

Organometallic derivatives of nickel at the zero oxidation stage in conjunction with certain organic halides were also used to initiate free-radical polymerization of styrene (St) and MMA. Initiation is based on the one-electron transfer oxidation of Ni(0). Block copolymers of St and MMA were successfully prepared by this process [18]. Because of the high affinity of the transition metal toward hydrogen, β -hydrogen elimination from a growing radical occurs and the unsaturated chain ends are formed, as was observed in free-radical polymerization of acrylic monomers using Co^{2+} as chain transfer agents [19,20]. This the major drawback of the transition-metal-initiating systems which deviates from the living polymerization.

B. Chitosan Mediated Living Polymerization

It is known that a growing end radical is generally accompanied by a termination and transfer reactions. In order to obtain a living system, those steps must be controlled or eliminated. There are two methods of stabilizing the growing end radicals and of controlling the approach of the end radicals. Examples of the stabilization of the growing end radical demonstrated by Robert et al. [21], which include a stabilized radical in perfluoro-2,5-diazahexane-2,5-dioxyl and a living copolymerization of hexafluoropropylene. The production of living growing end radicals was demonstrated by several workers and is limited to the specific polymerization systems (e.g., heterogeneous polymerization system [22], emulsion polymerization [23], clathrate polymerization system [24], high polymer association polymerization system [25], and coordination radical polymerization system).

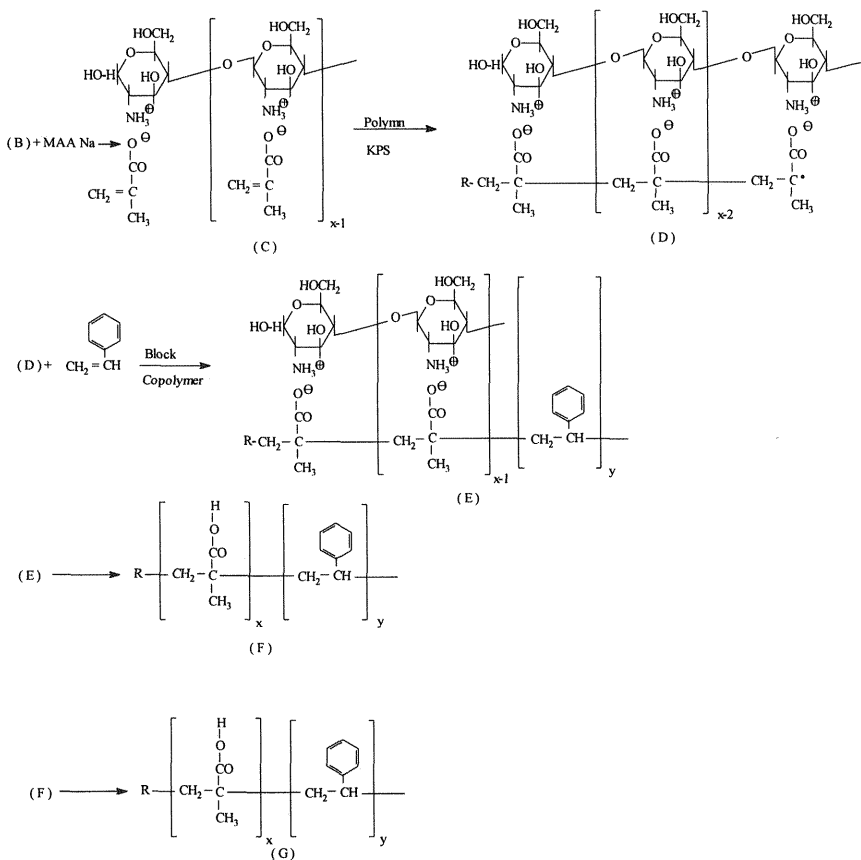
The stereo radical polymerization initiated in the sorbic acid in chitosan (A) solution and sodium methacrylate in chitosan acetate salt (B) solution was demonstrated by Kataoka and Ando [26]:



The living radical polymerization of sodium methacrylate [27] was kinetically investigated in aqueous solution in the presence of chitosan acetate using K_2SO_4 as an initiator. The molecular weight of poly(methacrylic acid) (PMA) obtained at a temperature $>60^\circ C$ with low initiator concentration increased linearly with increasing conversions. The polymerization proceeded with rapid initiation, successive propagation, and no termination. These results, as well as end-group analysis of PMA, indicated that initiation occurred at reducing end groups of chitosan and that the propagation reaction proceeded among methacrylate molecules bound to chitosan molecules by ionic and hydrophobic binding. It was also found that the molecular weight of PMA depends on molecular weight of chitosan used as a template [28].

The existence of living growing end radicals in the radical polymerization (MA-Na) in the presence of chitosan acetate salt has been ascertained by preparing block copolymers [29] with styrene as secondary comonomer. When polymerization of MA-Na reached about 93% conversion after 145 hr at $30^\circ C$, styrene was added to the system, which underwent further polymerization. The reaction steps are shown in the Scheme 1.

It reveals that the polymerization of MA-Na in chitosan acetate salt solution terminates when most of the MA-Na has been consumed, that the conversion of styrene increases with time, when styrene is added to the



Scheme 1

polymerization system for secondary polymerization. The growing end radicals are still living in the polymerization system. It has been shown [29] by the results of the above-mentioned block copolymerization of the polymer segment of chitosan acetate-MA-Na with styrene that the AB-type block copolymer can be easily obtained with excellent yield; in other words, active radicals at the growing ends produced in the polymerization of chitosan acetate-MA-Na are mentioned in the polymer.

Kataoka [30,31] also studied the polymerization of acrylic acid derivatives using potassium persulfate as the initiator and chitosan as template. The rate of radical polymerization reached a maximum at a MA·Na-chi-

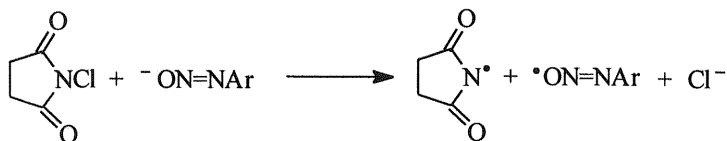
tosan acetate molar ratio of approximately 1:1. The polymerization rate in the presence of equimolar quantity of MA:Na–chitosan was proportional to $[K_2S_2O_8]$ and $[monomer]$ at initiator concentrations $< 3.5 \times 10^{-3} \text{ mol L}^{-1}$. The molecular weight of the polymer obtained increased proportionally to the conversion up to approximately 100%. Sulfate and/or sulfonate end groups in the polymer were approximately one per chain. The polymerization showed the characteristics of living polymerization.

C. Living Radical Polymerization by Oxygen-Centered Species

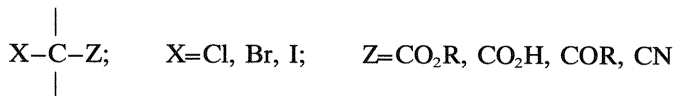
A new series [32] of electron transfer initiators has been shown to give rise to long-lived oxygen-centered radical species attached to propagating acrylate and methacrylate chain ends. The long-lived nature of these chain ends makes it possible to prepare block copolymers in some cases. The oxygen-centered radical species are generated from hyponitrite, arenediazoate, or cyanate anions by reaction with electron acceptors such as arenediazonium ions or activated alkyl halides.

Initiating species containing oxygen-radicals can be generated in at least two ways. The first involves transfer between activated carbon–halogen compounds with arenediazoate anions. This gives rise to carbon-centered radicals which initiate monomer polymerization, and the arylazooxy radicals ($\cdot ON=NAr$) which are associated with the growing end of the chain.

Kornblum [33] showed that suitably activated alkyl halides undergo facile electron transfer when reacted with anions such as $(CH_3)_2C(NO_2)^-$, $C_6H_5S^-$, N_3^- , and 1-methyl-2-naphthoxide. *N*-Halosuccinimides also react with arenediazoate, hyponitrite, or cyanate anions in the presence of monomer to initiate polymerization, presumably in analogy to the reactions using arenediazonium ions:

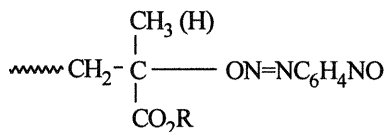


Living radical polymerization [32] would be expected to occur only when activated halides are used in conjunction with arenediazoates. Suitably activated halides contain at least one α -electron-withdrawing group, such as an ester, acid, ketone, or nitrile group:

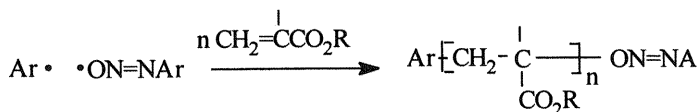
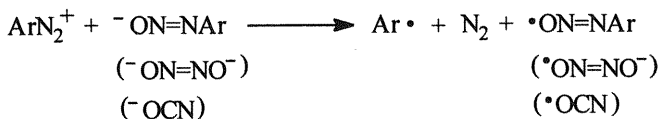


A reasonable rationalization is that inactivated alkyl halides react preferentially with $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{NO}^-$ to give relatively stable arylazo ether products [34].

Polymerization of acrylates and methacrylates [32] was studied at temperatures of 25–40°C. At these temperatures, it is reasonable that the C—O bond of the growing end of polymer chain, formed by radical recombination would be weakened to allow a terminal alkoxy group and would, thus, not exhibit living radical polymerization characteristics. Solomon et al. [35] have developed an analogous system involving $\cdot\text{ONR}_2$ radical end groups which is operative greater than about 80°C. The formation of the active initiating species for polymerization requires at least some intimate contact of the electron acceptors and oxyanions. This can be facilitated using small amounts of polar solvents.



The second method involves one-electron oxidation of arenediazoate, hyponitrite, or cyanate anions by reaction with arenediazoazodiazonium ions. Aryl radicals then initiate polymerization [32] of the monomer/methyl methacrylate, and the corresponding stabilized oxyl radical is associated with the growing end of the polymer:



Methyl methacrylate was radically polymerized using PhN_2BF_4 and NaN_2NO_2 . The polymer was purified by precipitation method. $^1\text{H-NMR}$ and first-atom bombardment mass spectroscopy showed that PMMA contains C_6H_5 groups.

The living nature of the polymerization was determined by correlating the number-average molecular weight (M_n) with conversion. M_n was found to increase with increasing conversion when polymerization was carried out with either arenedizonium ions or activated alkyl halides as electron acceptors. The other feature of the living nature of the polymerization was the ability to form the block copolymer. That was achieved by interrupting the polymerization (monomer removed under reduced pressure). The polymerization was continued by adding a second monomer to produce a block copolymer. For example, an A–B block copolymer [32] of MMA and butyl acrylate (BA) was prepared by reacting MMA with the initiator combination of $\text{C}_6\text{H}_5\text{N}_2\text{BF}_4$, $\text{Na}_2\text{N}_2\text{O}_2$, and CH_3OH at 30°C for 3 hr. Unreacted MMA and methanol were removed under reduced pressure. Then a portion of the PMMA was reacted with BA and a small amount of acetone at 30°C for 3 hr to yield a copolymer containing a BA/MMA ratio of about 1/4 (based on $^1\text{H-NMR}$). It should be pointed out that broad polydispersities ($M_w/M_n > 2.0$) and low conversions were obtained by using the above-described initiating systems, which decrease the living nature of these polymerizations.

D. Oxidized Polypropylene–Amine System

The possibility of obtaining a long-lived polymer radical was first reported by Melville [36] when either methyl methacrylate or chloroprene was polymerized photochemically in the gas phase. The resulting polymeric products deposited on the walls of the reaction vessel as fine particles was found to contain trapped free radicals which could be used to initiate subsequent polymerization of a second monomer in the absence of any further illumination.

In emulsion polymerization, the locus of the propagation reaction is within latex particles formed during the early stages of the reaction. The radicals in these particles remains active indefinitely until a new radical enters to cause termination, and if this entry is prevented or delayed, long-lived radicals would result. Mikulasova and co-workers [37,38] found that this situation could be arranged using a polymeric initiator and amine activator.

The existence of living polymer radicals in emulsion polymerization of styrene [37] in the presence of oxidized polypropylene and triethylene tetraamine was ascertained by preparing a MMA–St block copolymer. Polymerization of styrene proceeded after removal of the initiator from the

emulsion, reached to 100% conversion, and methyl methacrylate newly added to the system underwent further polymerization. The molecular weight of polystyrene and a MMA–St block copolymer increased with the conversion.

The kinetics of living radical polymerization of styrene in emulsion polymerization initiated by polypropylene hydroperoxide with triethylene tetramine was studied by Mikulasova et al. [38]. They proposed a two-stage mechanism. In the first stage, fast initiation and propagation occur on the surface of the polypropylene. In the second stage, continuous chain propagation without termination proceeds in polymer particles in the emulsion. The dependence of the rate and degree of polymerization on reaction time, initiator, and activator concentrations predicted by the kinetics were confirmed experimentally. Each polymer particle in the emulsion probably consists of one polymer molecule with a living chain end. Prerequisites for the living nature of this system are probably fast and/or limited decomposition and heterogeneity of the initiator in the emulsion polymerization.

In their investigation, Mikulasova and co-workers [37,38] reported that by using insoluble polymeric hydroperoxide with amine activators as the surface of free radicals, the hydroperoxide could be applied to the initiation reaction only at the beginning of the polymerization process. It was found that the decomposition of hydroperoxide which occurred only in the presence of radicals remained constant during the polymerization after removal of the polymeric initiator from the system by filtration. They demonstrated this effect by showing that the molecular weight of polystyrene continuously increased with conversion, and the molecular-weight distribution was narrow. Mikulasova and co-workers [37] used the polymeric-initiator concept for the preparation of diblock copolymers of styrene and MMA and obtained 97% yield of the block copolymer. The same initiator (i.e., isotactic polypropylene hydroperoxide as the initiator together with triethylene tetramine as an activator) was used by Bigdeli et al. [39] for the preparation of ABA triblock copolymers of styrene (A) and *p*-*tert*-butylstyrene (B) to obtain 100% conversion in each step of the reaction and an 80% overall yield of triblock copolymer after extraction.

Polymerization of styrene continued after removal of the initiator from the emulsion by filtration and eventually reached 100% conversion after 4 hr at 35°C. Monomers were added successively to the system, with each polymerization reaction carried to 100% conversion before the next monomer was added. Thin-layer chromatography was used to separate the homopolymers with block copolymers in order to determine the purity of the product. The existence of two separate phases in the extracted block copolymer was indicated by the observation of two distinct glass transition temperatures.

E. H_3PO_4 Complexing Agent

Olenin et al. [40] have reported the living graft copolymerization of acrylic and methacrylic monomers. In the presence of complexing H_3PO_4 , graft copolymerization of methyl methacrylate (MMA) and α -chloroacrylate on cellophane film irradiated with x-rays follows a living mechanism. Under given initial grafting conditions and at a constant number of grafted chains, the yield of grafted polymer and the molecular weight of grafted chains are proportional to the time of contact of the irradiated film with the reaction mixture. The effect of the composition of the H_3PO_4 –MMA mixture on the yield and the molecular weight of the grafted polymer was determined and the chain propagation rate constant (approximately $10 \text{ L mol}^{-1} \text{ sec}^{-1}$) for polymerization of MMA on irradiated cellophane was established. In addition to simple graft copolymers, diblock and triblock graft copolymers of controlled block lengths were prepared by sequential introduction of the desired monomers.

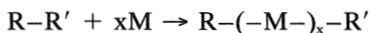
Tillaev et al. [41] have reported on the controlled systems of graft copolymers of cellulose triacetate by living radical polymerization. In the grafting of MMA on γ -ray-irradiated cellulose triacetate in the presence a H_3PO_4 complexing agent, the degree of grafting increased from 2.1% to 25% by increasing the reaction time from 5 to 60 min. Similarly, the molecular weight was increased from 1.95×10^6 to 3.3×10^6 . The grafting yield increased linearly with increasing irradiation dose, whereas the molecular weight of grafted chains did not decrease. Comparing the concentration of radicals formed by irradiation with the number of grafted chains showed that 3.0–21.0% of radicals formed are involved in grafting, depending on reaction time.

F. Iniferter Techniques

The propagating radicals in the homogeneous radical polymerization systems are very short-lived, it is impossible to obtain long-lived and propagating radicals, except its mobility is decreased markedly [42,43]. Therefore, a long-standing goal has been the development of a living polymerization in homogeneous solution, which had been considered to be unlikely. In 1982, the concept of iniferter (initiator–transfer agent–terminator) was proposed by Otsu and Yoshida [42] for the design of the polymer chain end structure and Otsu et al. used some iniferters to propose a model for living radical polymerization in a homogeneous system [43].

The concept of iniferter may be summarized as follows: The polymer formation in the radical polymerization of a monomer (M) by an initiator

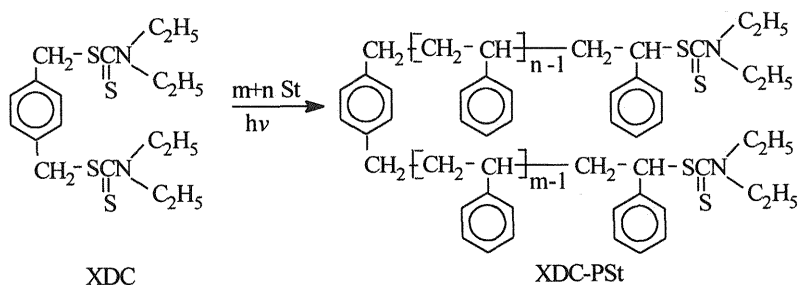
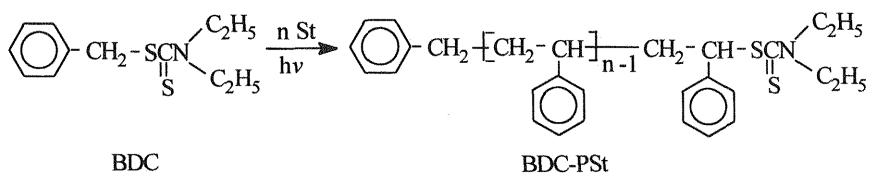
(R-R') may be expressed as follows, by considering ordinary bimolecular termination:



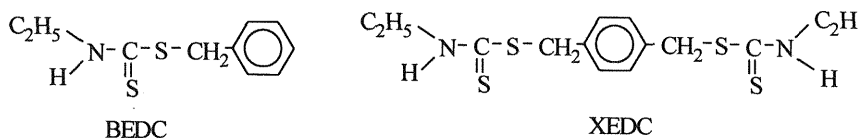
In this case, radical polymerization gives a polymer with two initiator fragments at its chain ends. In radical polymerization, termination by disproportionation and charge transfer (CT) reactions are known to be important. In these cases, the number of the initiator fragments per polymer molecule is always <2. But in cases where the initiators have very high reactivities for CT reactions to the initiator and/or primary radical termination, it is expected that a polymer with two initiator fragments at its chain ends will be obtained. Such initiators are considered as iniferters as proposed by Otsu and Yoshida [42]. From the preceding definition, the iniferters can be classified into various types, such as monofunctional iniferter, bifunctional iniferter, and polymeric iniferter or macroiniferter. Among the iniferters used, some sulfur compounds having *N,N*-diethyldithiocarbamate groups were found to serve as excellent photoiniferters for the controlled synthesis of various monofunctional telechelics [44], block [45–49], star [50], and graft [51] polymers.

1. Photoiniferters

In an earlier article, Otsu et al. [48] have reported on the living radical polymerization of styrene and methyl methacrylate (MMA) in homogeneous system by using photoiniferters. Benzyl *N*-ethyldithiocarbamate (BEDC) and xylene bis(*N*-ethyl-dithiocarbamate) (XEDC) were used as photoiniferters. The polymers obtained by BEDC and XEDC had one and two reactive *N*-ethyldithiocarbamate end groups, respectively. When these polymers were reacted with nucleophiles and copper (II) ion, the chain extension reactions were observed to occur depending on their functionality. By using the polymers obtained by BEDCH and XEDCH as monofunctional and bifunctional polymeric photoiniferters, the AB and ABA block copolymers were also obtained respectively. Similar results were obtained by using benzyl *N,N*-diethyl dithiocarbamate (BDC) and xylene bis (*N,N*-diethyl dithiocarbamate) (XDC) as monofunctional and bifunctional photoiniferters, respectively. These photoiniferters consisted of identical bonds. BDC and XDC were used as monofunctional and bifunctional photoiniferters for the living polymerization of styrene and methyl methacrylate [46], respectively. Polymers having identical chain end groups were formed as follows:



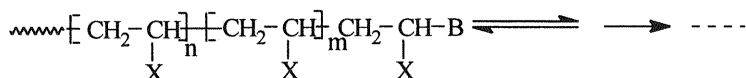
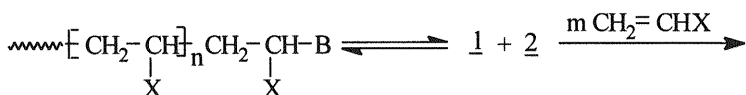
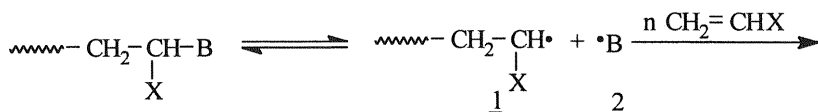
BEDC and XEDC were also prepared and used as photoiniferters [48] for the polymerization of St and MMA. The structures of these photoiniferters are as follows:



Polymerizations were carried on in a sealed glass tube at 30°C under irradiation of a Toshiba SHL-100 UV lamp from a distance of 10 cm.

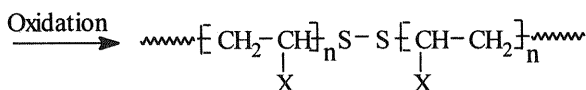
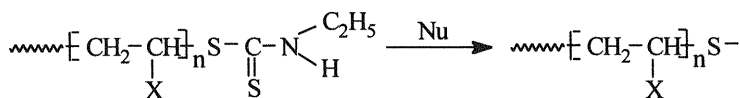
The yield and the molecular weight (M_n) of the polymers formed are observed to increase as a function of reaction time, indicating that the polymerization proceeds via a living radical mechanism in a homogeneous system. The conversion was about 30% after about 15 hr of polymerization in the case of St. For MMA polymerization, the conversion was about 60% after 12 hr for BDC or XDC initiators. But the conversion was only about 30% after 12 hr for the BEDC or XEDC initiator. To further confirm the living nature of these polymerization systems, Otsu et al. [48] determined the number of end groups of the polymers produced in photopolymerization of St with BDC and XDC initiators. The number of $(\text{C}_2\text{H}_5)_2\text{NCSS--}$ end groups per one polymer molecule are found to be almost constant (i.e., 1 and 2 for BDC and XDC, respectively), independent of the reaction time. These results strongly suggest that the polymerization with BDC and XDC proceeds via a living monoradical and biradical polymerization mechanisms, respectively, according to the following model. To demonstrate the mecha-

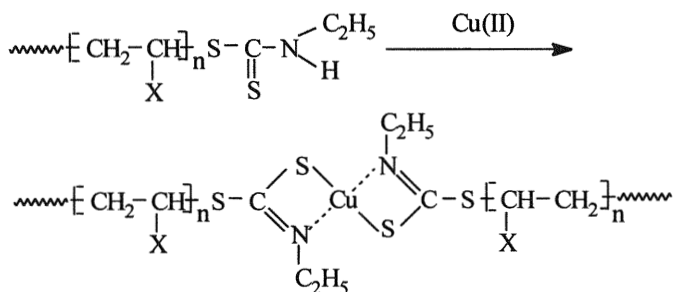
nism, Otsu et al. [51] proposed a model for living radical polymerization in a homogeneous system by using phenylazotriphenyl methane and tetraethylthiouram disulfide as thermal and photoiniferters, respectively. This idea was that a short-lived unstable radical including a propagating radical only exists as its dimer consisting of a covalent bond, and if this bond can dissociate, the unstable radical may be supplied into the system. The model can be expressed as follows:



If the propagating chain end which can dissociate thermally or photochemically into a propagating radical (1) and a small radical (2), which must be stable enough not to initiate a new polymer chain, and can recombine easily with a propagating radical and if these dissociation, monomer addition, and recombination cycles are repeated, such a radical polymerization proceeds apparently via a living mechanism.

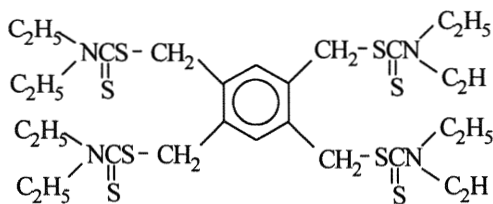
Nakagawa and co-workers [52] have reported that *N*-ethyl-dithiocarbamate ester groups in polystyrene can be hydrolyzed by nucleophiles such as sodium hydroxide and dimethylamine to the thiol group, which is then oxidized to form chain extension reactions. It can also form a chelate bond with divalent metal ions such as a Cu(II) ion. If these reactions are applied to monofunctional and bifunctional monomers obtained by BEDC and XEDC photoiniferters [47], the following chain extension reactions will occur:





The chain extension of polymers occurred through a disulfide bond formation. When monofunctional polymer obtained by BEDC was used, the molecular weight of the polymer obtained after the chain extension reaction increased about two times compared with the starting polymer. However, with the increase of chain extension reactions of bifunctional polymers obtained by XEDC, the molecular weight increased about three to five times. Similar results were obtained for chain extension reactions by a chelate bond formation.

In previous articles [45,47], it has been reported that AB and ABA block copolymers are easily synthesized through living radical polymerization using polymeric photoiniferters obtained from BDC and XDC as monofunctional and bifunctional photoiniferters. This technique was applied to the synthesis of a variety of block copolymers consisting of three- or four-component systems [53]. The use of a tetrafunctional photoiniferter [i.e., 1,2,4,5-tetrakis (*N,N*-diethyl dithiocarbamyl (methyl)benzene (DDC)] has been reported [49] to synthesize star polymers of MMA. The structure of DDC is given in the following scheme.



DDC

The tetrafunctional photoiniferter (DDC) was prepared by the reaction 1,2,4,5-tetrachloromethylbenzene with sodium *N,N*-diethyl-dithiocarbamate in ethanol at room temperature for about 24 hr and recrystallized from a benzene/*n*-hexane mixture (~1:1 v/v); the melting point is 125.5–126.3°C. Photopolymerization of MMA with the tetrafunctional iniferter (DDC) was compared with the bifunctional iniferter (XDC) and the monofunctional in-

iferter (BDC). For purpose of comparison, the polymerization was carried out using these iniferters, in which the concentration of *N,N*-diethyl-thiocarbamate group was kept constant:

$$[\text{BDC}] = \frac{1}{2}[\text{XDC}] = \frac{1}{4}[\text{DDC}]$$

The time-conversion relations observed for all of these photoiniferters are identical to one another; that is, the polymer yields increased linearly with polymerization time. The conversion was about 3% after 7 hr of polymerization. These results indicate that these three kinds of *N,N*-diethyl-dithiocarbamate groups show identical reactivity for radical polymerization. The molecular weight of the polymer was increased as a function of reaction time, indicating that these polymerizations proceed via a living mechanism. The relative ratio of molecular weight was 1.0:1.7:2.5 for BDC, XDC, and DDC, which was different from the ideal case of 1:2:4. These results were in agreement with the results described in the earlier article of Otsu and Kuriyama [45]. This indicates that the polymerizations of MMA by BDC and XDC do not proceed according to the ideal monofunctional and bifunctional mechanisms strictly, probably owing to self-termination [54].

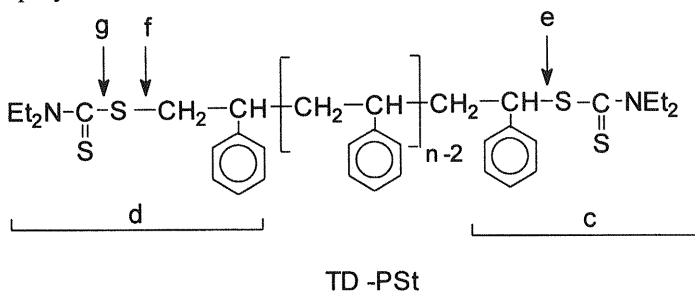
Among the iniferters used, some compounds containing *N,N*-diethyl-dithiocarbamate groups were found to be excellent photoiniferters of living radical polymerization. Otsu et al. [55] summarized these ideas and discussed some characteristics of the living radical polymerization with tetraethylthiuram disulfide (TD), benzyl *N,N*-diethyl-dithiocarbamate (BDC), *p*-xylene bis(*N,N*-diethyl-dithiocarbamate (XDC), and tetrakis(*N,N*-diethyl-dithiocarbamayl) benzene (DDC) as photoiniferters.

Many studies were carried out for the radical polymerization of St or MMA with TD by Ferington et al. [56], Otsu et al. [57–60], and Barton and Bevington [61,62] to clarify the mechanism. The results obtained by these workers are summarized as follows:

- TD is a weak radical initiator with retarding properties.
- Primary radical termination and chain transfer reactions to TD are important.
- The resulting polymer has two $\text{Et}_2\text{NCSS-}$ groups at its chain ends [59].
- This end group can act further as a photoinitiator to give block copolymers [63–65].

Otsu et al. [55] reexamined these results in order to enable the design of the polymer structure. The number-average molecular weight increased linearly with conversion during the polymerization of St at 30°C using TD and BDC as the photoinitiator, indicating that these polymerizations proceed

by a living radical polymerization mechanism. The M_w/M_n polydispersity values were broad and also increased linearly with reaction time. However, the number of $\text{Et}_2\text{NCSS-}$ end groups of TD-PSt still remained constant (about two). This was found to serve as a good polymeric photoiniferter for the polymerization of vinyl monomers such as St and MMA. In case of photopolymerization of MMA with TD-PSt, the yield and M_n of the polymers increased with reaction time, and the block copolymer was obtained efficiently. From these results, it was claimed that these polymerizations proceed via a living radical mechanism. These results suggest that TD served as a difunctional photoiniferter for the styrene polymerization and that the photodissociation of the (d) end $\text{Et}_2\text{NCSS-}$ group occurred at the C-S bond (f) giving $\text{C}_6\text{H}_5\text{CHCH}_2\cdot$ and $\text{Et}_2\text{NCSS}\cdot$, which are effective for living radical polymerization. The scheme is as follows:

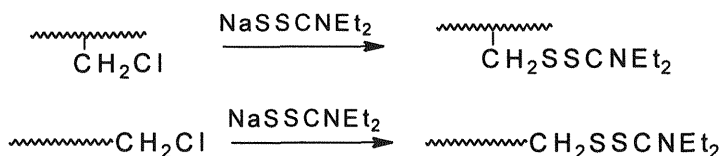


As described above, the polymers obtained with BDC and XDC were expected to function as monofunctional and difunctional macrophotoiniferters, respectively, to give the AB and ABA block copolymer, and TD acted as a difunctional iniferter in the polymerization of St. The yields of block copolymers obtained by TD-, BDC-, and XPDC-PSt were high (>70%) and ABA, AB, and ABA block copolymers, respectively, were obtained, except in the case of TD-Pst/MMA and EA which gave an AB block copolymer. In relation to this result, the observed iniferter activities of BDC-PMMA and XDC-PMMA toward St were low as compared with that of BDC-PSt and XDC-PSt to MMA and EA, probably indicating that the $\text{Et}_2\text{NCSS-}$ end groups in PMMA do not function as a good iniferter, as described by Otsu et al. [48] in a previous article.

Otsu et al. [48] have also reported a solid-phase block copolymer synthesis using a PSt-gel photoiniferter; that is, the $\text{Et}_2\text{NCSS-}$ group attached to PSt-gel through a hydrolyzable ester spacer was prepared and used as a photoiniferter of the polymerization of St. The resulting grafted PSt onto PSt-gel acted as a macroiniferter for radical polymerization of MMA. In this way, a homopolymer of MMA was easily separated from the graft-block copolymer attached to PSt-gel. Hydrolysis of the latter yielded a

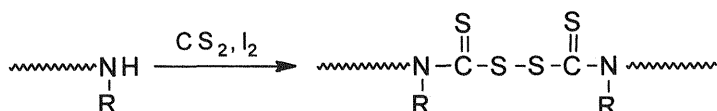
block copolymer of St and MMA with 10–15% homopolystyrene. This procedure was similar to that described for the solid-phase peptide synthesis using a reagent attached to the polymer support [66]. The homopolystyrene formation can be avoided by the addition of TD, which can dissociate to *N,N*-diethyl-dithiocarbamate radicals, to the photopolymerization of St. Using the solid-phase iniferter technique, various diblock, triblock, and multi-block copolymers possessing PSt, PMMA, poly(ethyl methacrylate), poly(*p*-chlorostyrene), and poly(*p*-methoxy styrene) were prepared. Apart from acrylic- and vinyl-type polymers, many other polymers including siloxanes [67–70], polyurethanes [71], polyolefines [72,73], polyvinylchloride [74–77] were used as polymeric photoiniferters for the preparation of block and graft copolymers. These studies were recently reviewed by Kumar et al. [13] and will not be discussed in detail here. The general strategy for the preparation of polymeric iniferters is as follows:

- (a) Use of a low-molar-mass iniferter in the polymerization of a monomer and the resulting polymer chain, terminated by an iniferter group, become a polymeric photoiniferter capable of further reaction with a new monomer to produce a block copolymer.
- (b) Displacement of chlorine atom, attached to polymers as side and terminal groups, by sodium diethyl-dithiocarbamate gives a polymer which can be subsequently grafted or blocked respectively:



Substitution of chlorine by dithiocarbamate takes place at temperatures between about 50°C and 90°C in a solvent such as toluene, xylene, or ethyl acetate under nitrogen. In some cases, displacement groups other than chloride including bromide, tosylate, and mesylate were also used.

- (c) Reaction of secondary amines attached to polymers with CS₂ and I₂. This should lead to the formation of a mid-chain functional polymer and the resultant polymer acts as an inner macroiniferter:



Liu et al. [78] have also reported on the living photopolymerization of St using BDC as the photoiniferter. Both the yield and average molecular weight of the polymer increased with increasing polymerization time. Polymers with functional end groups were obtained. During the polymerization, the stable small radical which was produced by photolysis of BDC or functional end groups and the propagating radical of St were determined by ESR.

2. Ultrasonic Irradiation

Liu et al. [79] have reported on the polymerization of St, initiated by a polymeric iniferter such as diethyl-thiocarbamate-terminated PSt under ultrasonic irradiation. The ultrasonic polymerization of St in the presence of polymeric iniferter proceeded via a living radical polymerization mechanism in which initiating polymeric radicals were generated by ultrasonic cleavage of the terminal groups of the iniferter. Much attention has been paid to the effect of high-intensity ultrasonic irradiation of polymers in solvent, and the degradation of the polymers has been observed and investigated comprehensively. Some workers [80] have shown that a polymer with a small portion of weak linkages (e.g., O-O), which were introduced into polymer chains during polymerization, degraded much faster, and almost all of the weak linkages were broken. As described in the previous section, BEDC acts as iniferter for the living radical polymerization [43,47]. Similarly, a polymer with an ethylaminothiocarbonyl end groups can also be used as a polymeric iniferter, in which the linkage between the polymer chain and the chain end groups is rather weak. When such a polymeric iniferter solution was irradiated by medium intensity ultrasonic waves, the majority of the chemical bonds in the polymeric iniferter would not be affected while the C-S bonds in the polymeric iniferter would dissociate, producing one propagating radical as well as one stable thiyl radical; then the polymerization of St would be initiated [79].

The polymerization of St proceeded smoothly at 47°C using a polymeric iniferter under ultrasonic irradiation [79]. It was shown that only a portion of the polymeric iniferter was consumed during ultrasonic irradiation. The degree of polymerization (DP) increased as a function of the reaction time, indicating that the polymerization proceeded via a living ("living" radical polymerization in this case meaning that the radicals can continuously be regenerated, but their individual life cannot persist throughout the experiment [79]) radical polymerization in a homogeneous system. During the ultrasonic irradiation, the mechanical forces exerted on the polymer chains, or high temperature at a given locality, must have led to the dissociation of the weaker linkage between the polymer chain and the end group in the polymeric iniferter, producing a propagating radical and a stable

radical. Under continuous ultrasonic irradiation, these dissociation, propagation, and recombination processes would be repeated. It is apparent that such a radical polymerization proceeds via a kind of “living” radical mechanism.

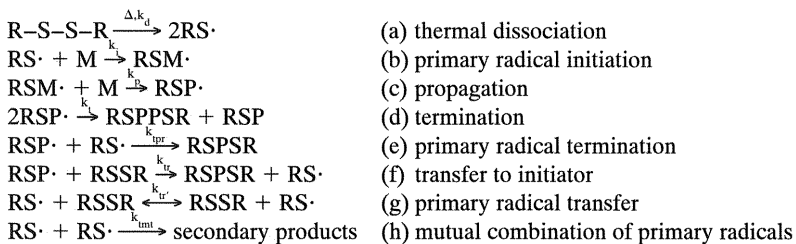
3. Thermal and Redox Systems

Thiuram disulfides, described above as photoiniferters, can also act as thermal iniferters. The mechanism of the polymerization is the same and polymer chains are invariably end-capped at both ends with iniferter segments. The use of thiurams as thermal or photoiniferters for the preparation of block copolymers greatly depends on the quantum yield of dissociation. The synthesis of dithiocarbamate functional polymers by direct photolysis of the iniferters is limited due to the low quantum yield of dissociation, especially in the case of the thiuram disulfide (e.g., the quantum yield of dissociation (ϕ_d) of TD is 0.0025 in cyclohexane [81]). This very low value makes the photochemical dissociation much less attractive than the thermal one. It was suggested that better dithiocarbamate functionalization can be achieved by either thermal initiation with TD at 95°C or polymerization in the presence of AIBN as a thermal initiator and TD as a chain transfer agent. In the latter case, monofunctional or bifunctional TD–PSt were formed, depending on the mole ratio AIBN/TD. Interestingly, the quantum yield of BDC was found to be 0.06, which is 24 times higher than that of TD. Thus, BDC can be used both as a thermal initiator and as a photoiniferter [81].

As iniferters, the thiuram disulfides follow unusual kinetics and cannot be explained within the framework of the traditional view of kinetics and mechanisms of the free-radical polymerization. The special features of the iniferter process can be summarized as follows:

- Continuous growth of the molecular weight is observed. The number-average degree of polymerization is normally known to increase linearly with the conversion.
- The rate of polymerization, at low conversions, either is constant or, at first, decreases with time and then later levels off and thereafter remains unchanged.
- The number of iniferter molecules in the polymer hardly changes with conversion from a certain point in time.
- Polymers obtained can act as macroinitiators which are capable of initiating further polymerization.

Nair and Clouet [82] investigated the kinetics of the polymerization on the basis of the following general scheme of elementary reactions of radical polymerization conducted in the presence of iniferters:



The terms k_p , k_t , and so forth, are the rate constants for the respective reactions. The kinetic scheme resembles that of a free-radical copolymerization between the monomer M and the thiuram disulfide ($RSSR$) considered as a second monomer, and a kinetic expression for a conventional radical copolymerization can be suitably applied to this system when the termination is chemically controlled (as it is for low conversion). Thus, the rate of polymerization can be written as follows:

$$R_p = \frac{k_p}{k_{tr}} [M] R_i^{1/2} / \left[\frac{k_t}{k_{tr}^2} [M]^2 + \frac{2k_{tr}}{k_{tr}k_t} [M][RSSR] + \frac{k_{mt}}{k_i^2} [RSSR]^2 \right]^{1/2}$$

which can be arranged as

$$R_p^2 = A^2 [M] 2[RSSR] / \left(1 + 2B \frac{[RSSR]}{[M]} + C \frac{[RSSR]^2}{[M]^2} \right)^{-1}$$

where A , B , and C are complex constants

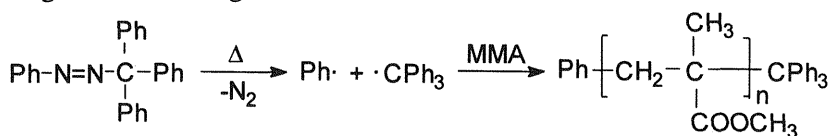
$$A = \frac{k_p}{k_i^{1/2}} (2fk_d)^{1/2}, \quad B = \frac{k_{tr}k_{tr}}{k_i k_t}, \quad C = \frac{k_{mt}}{k_i} \left(\frac{k_{tr}}{k_i} \right)^2$$

In this complex equation, the rate of polymerization is no longer linear with respect to the square root of the initiator concentration. The equation predicts that the rate increases with the iniferter concentration at the beginning, reaches a maximum, and then decreases.

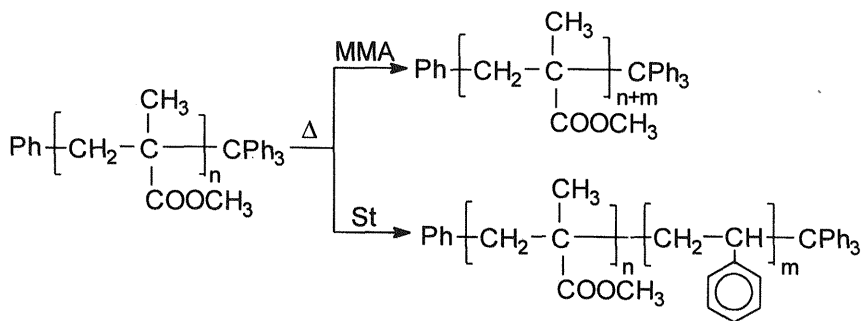
The kinetic behavior of iniferter polymerization exactly follows the path predicted by the preceding equation. The unusual kinetic behavior of this polymerization was first noticed by Ferington and Tobolsky [83], and a kinetic expression with a graphical method evaluation was introduced by Beniska et al. [84,85]. A more rationalized kinetic study using functional iniferters along the lines of Staudner was performed by Nair and Clouet [86,87] by using computerized multiple regression analysis, which eliminated several errors associated with Staudner's technique [84,85] and led to a direct estimation of various kinetic parameters. Recently, Kuchanov [88] studied the kinetics of this process over the whole range of monomer

conversion. Based on the published experimental data, he developed the simplest variant of the quantitative theory of iniferter polymerization. Conditions for kinetic parameters were formulated whose fulfillment predetermines that radical polymerization occurs according to the iniferter mechanism.

Apart from thiuramdisulfides, some other compounds were shown to be useful thermal iniferters. Otsu and Tazaki [89] showed that compounds of the phenylazotriphenylmethane type can act as a thermal iniferter, where the phenyl radical initiates the polymerization, and the triphenylmethyl (trityl) radical is a stable radical which couples with the growing chain, exhibiting a kind of living radical nature:



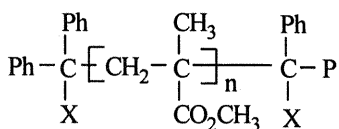
Upon heating, the active chain end group (the tritylic end) undergoes reversible dissociation. The molecular weight of the polymers obtained increased with conversion, claimed as evidence for the living nature. The trityl end-capped and isolated polymer can serve as a macroiniter for the subsequent polymerization which leads to chain extension and block copolymer formation:



It was shown by Demircioglu et al. [90] that trityl functionalized polymers prepared by other means (i.e., chain transfer reactions) can also function as a macroiniter.

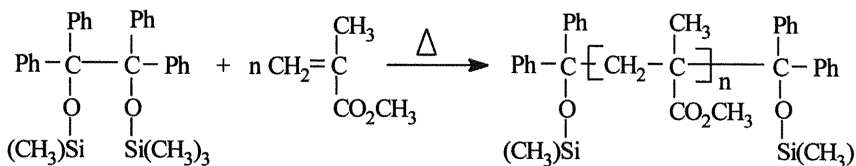
Such polymerizations were also reported with other thermal iniferters such as highly substituted ethanes and silyl pinacol ethers. It was shown [91] that sterically hindered carbon-carbon single bonds such as those found in hexaphenylethane were easily thermally cleaved to produce trityl radicals. Subsequently, it was found that the tetraarylethane and benzpinacol could also decompose in the same way and could be used [92,93] as initiators for

free-radical polymerization. The initiating characteristics of various tetraphenylethanes toward MMA and St were reported by Bledzki and Braun [94,95]. These compounds dissociate thermally into two diphenylmethyl radicals which either add to the monomer molecule or combine with a growing radical. This primary radical termination is the main termination reaction in the first step, and oligomers which carry a diphenyl group at each end of the chain are formed thereby, as shown by the following for the MMA polymerization:

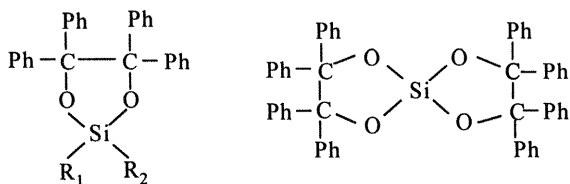


In the second step, when almost all of the initiator is consumed, these oligomers can reinitiate the polymerization by thermal cleavage of the C—C bond which is formed in the primary radical termination reaction, giving a diphenylmethyl radical and a growing chain radical.

Some workers [96–98] have made use of bistrialkylsilylether derivatives of benzpinacol to behave both as initiators and terminating agents in a manner similar to substituted ethanes:



Polydimethylsiloxane–vinyl block copolymers were synthesized [97,98] by first preparing polydimethylsiloxane macroinitiators having benzpinacol bisilyl ether groups along the chain backbone which were then thermolyzed in the presence of vinyl monomers. Cyclic analogs of the open-chain benzpinacol bisilylethers of the following structures were also prepared and used for the same purpose [99]:



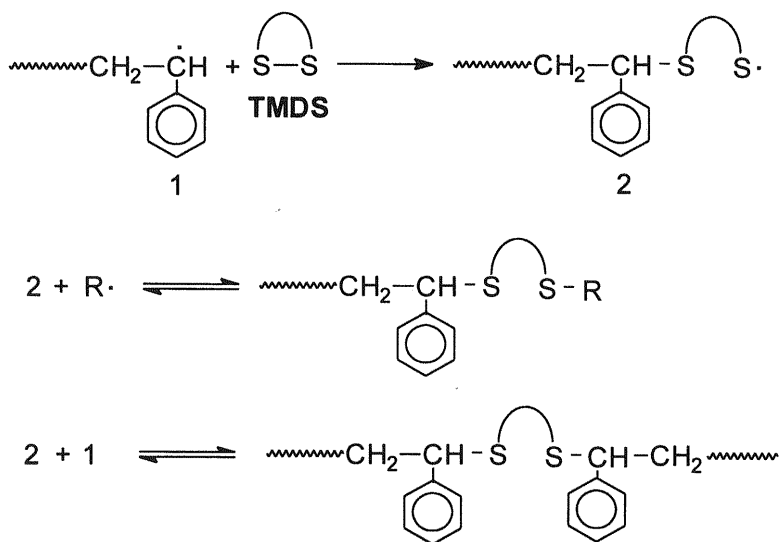
<u>R₁</u>	<u>R₂</u>
CH ₃	CH ₃
C ₂ H ₅	C ₂ H ₅
C ₆ H ₅	C ₆ H ₅
CH ₃	CH ₂ =CH
CH ₃	C ₆ H ₅
(CH ₃) ₃ C	(CH ₃) ₃ C

A good living system should require fast initiation, which is not fulfilled with these systems.

Recently, Endo et al. [100] found that the polymerization of St in the presence of a six-membered cyclic disulfide, tetramethylene disulfide (TMDS), proceeds with a living radical mechanism. The molecular weights of the polymers increased almost linearly with conversion. These authors considered the reactions shown in Scheme 2 to account for the living nature of the polymerization. However, some undesirable reactions for decreasing the living nature (e.g., an attack of the thiyl radical on the St monomer and bimolecular termination between styryl radical) cannot be excluded.

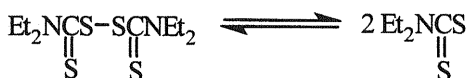
4. Two-Component Iniferter System

Recently, Lambrinos et al. [101] observed some deviation from the proposed polymerization mechanism in iniferter systems. These authors pointed out the bimolecular termination leading to the deactivation of the iniferter site in the polymerization of *n*-butyl acrylate initiated by *p*-xylene bis(*N,N*-diethyl-dithiocarbamate) and claimed that the polymerization was not strictly living. Doi et al. [102] proposed a new two-component iniferter system to prevent the deactivation of the iniferter site. In this system, BDC and TD act as an iniferter (or an initiator) and a chain transfer agent and/or a primary radical terminator, respectively. In the polymerization of methylacrylate (MA) with BDC bimolecular termination leading to the deactivation of the iniferter site occurred in preference to chain transfer to BDC and the dithiocarbamyl radical that produce the iniferter site, resulting in a deviation from



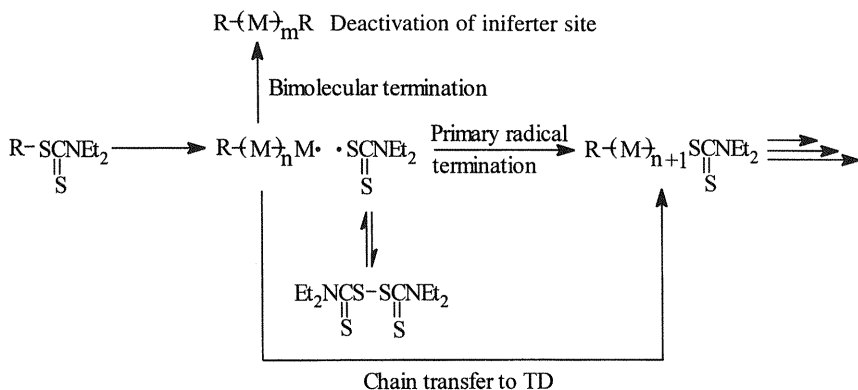
Scheme 2

the proposed mechanism. TD was added to the polymerization system to reproduce the iniferter site because it is an equilibrium with dithiocarbamyl radicals which can function as a primary radical terminator under UV irradiation:

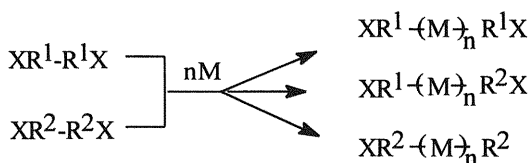


A chain transfer to TD is another effective route to reproduce the iniferter site at the chain end. Thus, the chain end of the polymers in the polymerization with BDC can be controlled in a high efficiency in the presence of TD. The overall process is depicted in Scheme 3. This two-component iniferter system was also applied [102] to the synthesis of a star polymer with DDC as a tetrafunctional photoiniferter.

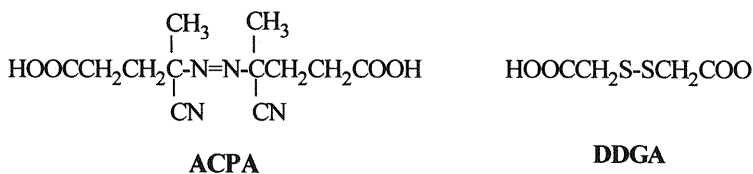
The two-component iniferter system was also used [103] to prepare telechelic polymers through radical polymerization. The system consists of two compounds bearing the same functional group, one being an initiator or an iniferter ($\text{XR}^1\text{-XR}^1$) and the other a chain transfer agent ($\text{XR}^2\text{-XR}^2$). Polymerization by using these compounds results in the formation of polymers having three types of end groups as follows:



Scheme 3



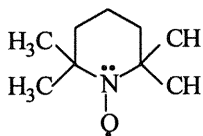
Polymerization of St and vinyl acetate by using 4,4'-azobiscyanopentanoic acid (ACPA) and dithiodiglycol acid (DDGA) as the initiator and the chain transfer agent, respectively, yielded polymers having a carboxyl group at both chain ends [103]:



G. Living Radical Polymerization in the Presence of Stable Free Radicals

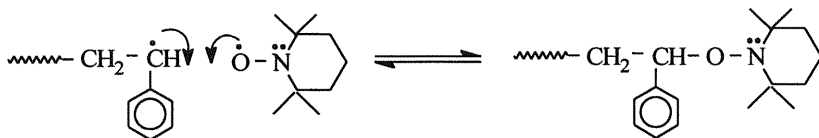
The concept of reversible termination by using a stable free radical has recently been shown to control growing free-radical chains [104,105]. The stable nitroxide radicals such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) are known to act as strong polymerization inhibitors [106,107]. In the mean time, nitroxides react at nearly diffusion-controlled rates with carbon-centered radicals, and the reaction rates are influenced by solvent

viscosity. Notably, oxygen-centered radicals do not participate efficiently in this process [108–110]:



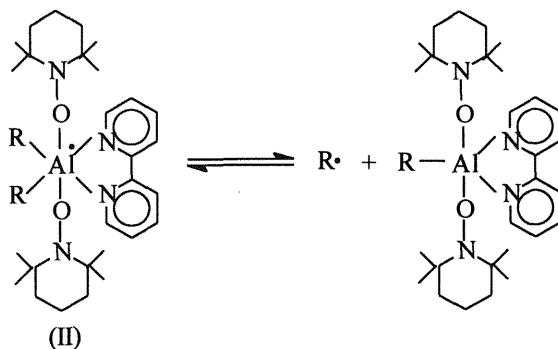
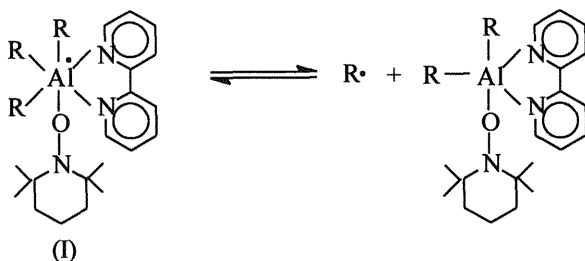
TEMPO (2,2,6,6-tetramethyl-piperidinyloxy)

The reaction of nitroxide radicals with growing polymer chains has been the subject of intensive investigation. According to an investigation of Solomon et al. [35] a nitroxide radical adduct can be used to initiate polymerization, whereas the nitroxide moiety can reversibly terminate the growing chain, producing low-molecular-weight oligomers:

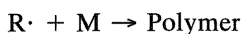


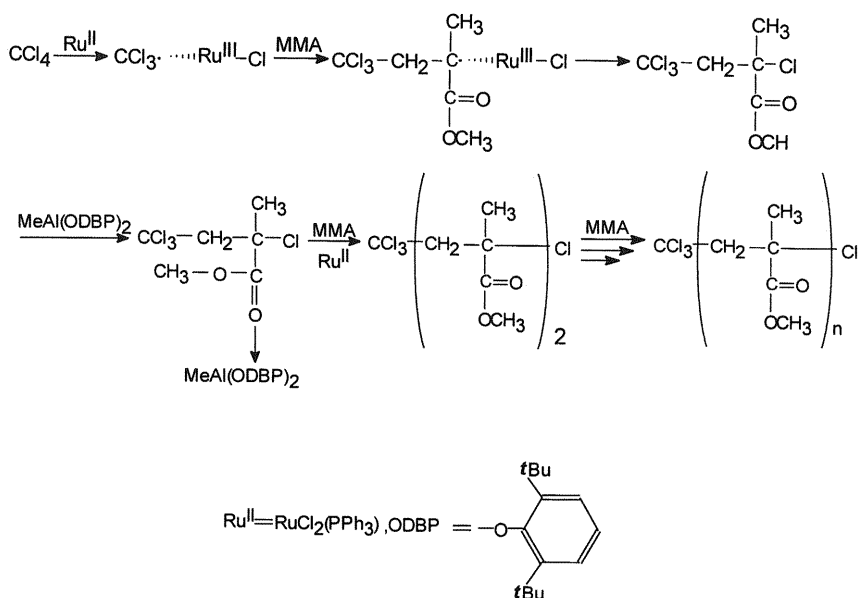
In this process, nitroxides function to form thermally transient adducts in a similar manner to the iniferters. Compared with the iniferter system, the use of nitroxides has the advantage of inhibiting but not initiating polymerization. Consequently, the stable free radicals are not capable of initiating new chains late in the polymerization process, as they reversibly react with a propagating chain. This polymerization system contains a monomer or monomer mixtures, free-radical initiator, and a stable free radical and requires only heating at elevated temperatures. Polymerization of styrene with benzoyl peroxide in the presence of TEMPO under argon at 95°C for 3.5 hr, followed by heating at 123°C for 69 hr yielded polystyrene with a polydispersity of 1.26. The polymeric chains were all initiated at about the same time, as was confirmed by GPC analysis (i.e., a narrow polydispersity was obtained early in the reaction). Moreover, the polydispersity remains constant throughout the polymerization, indicating a living type of mechanism. The molecular weight of polymers increased with increasing polymerization time. The narrow polydispersity was maintained even at high conversions. Similar results were obtained at much higher temperatures (e.g., at temperatures between 125°C and 150°C). This process can also be performed in suspension. A suspension copolymerization of styrene and butadiene with benzoylperoxide in the presence of TEMPO yielded a copolymer with a polydispersity of 1.36. Interestingly, the same polymerization system in the absence of TEMPO gave a copolymer with a polydispersity of 4.21.

An interesting variation of this method has recently been reported by Mardare and Matyjaszewski [110]. The initiating system involved persistent radical formation by ternary complexes of organoaluminum compounds with Lewis bases and stable radicals. These authors polymerized vinyl acetate (polymerizable only by radical mechanism), initiated by triisobutylaluminum ($\text{Al}(\text{iBu})_3$) complexed by a bidentate ligand, 2,2'-bipyridyl (Bpy), and activated by TEMPO. Molecular weights increased linearly with conversion. The dependence of molecular weights on conversion at different TEMPO/ $\{\text{Al}(\text{iBu})_3:\text{BPy}\}$ ratios was also studied. Molecular weights higher than theoretically calculated values at a low proportion of TEMPO indicated incomplete initiation which was attributed to the unavoidable reaction of the co-catalysis with moisture or oxygen. The increase in the proportion of TEMPO (e.g., at the ratio 3) did not cause the expected increase in the molecular weight (probably due to the contribution of chain transfer at this ratio). The real nature of the growing and dormant species is rather complex and not yet known. The authors assumed that the radicals cleaved homolytically from the dormant radicals (I and II) in the reversible mode.



Radicals $\text{R}\cdot$ are capable of initiation and subsequent propagation:



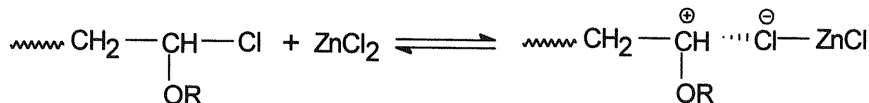


Scheme 4

Polymerization of vinyl acetate was also initiated in the absence of TEMPO at a very slow rate, but in a controlled manner. Chain extension can be achieved by new monomer addition, and block copolymers of styrene and methyl methacrylate were also prepared.

H. Living Radical Polymerization via Reversible Homolytic Activation of Carbon–Halogen Bonds with Metal Complexes

In the past 15 years, several new living cationic polymerizations, based on stabilization of unstable growing carbocations, have been developed. For example, living polymerization of vinyl ethers, initiated by protonic acid/vinyl halide combined system proceeds via reversible and heterolytic cleavage of a carbon–halogen terminal bond mediated by the metal halide [111]:



Recently, Kato and co-workers [112] extended this approach to free-radical systems. Polymerization of MMA with a ternary initiating system consisting of CCl_4 , $\text{RuCl}_2(\text{PPh}_3)_3$, and $\text{MeAl}(\text{ODDBP})_2$ yielded polymers with a fairly narrow molecular weight range ($M_w/M_n = 1.3\text{--}1.4$). Moreover, the molecular weight of polymers increased with the monomer conversion. A proposed mechanism is illustrated in Scheme 4. Controlled polymerization is achieved by the reversible activation of the growing carbon–chloride terminal by ruthenium compound aluminum Lewis acid. It is of note that no polymerization was observed in the absence of the three components CCl_4 , $\text{RuCl}_2(\text{PPh}_3)_3$, or $\text{MeAl}(\text{ODBP})_2$.

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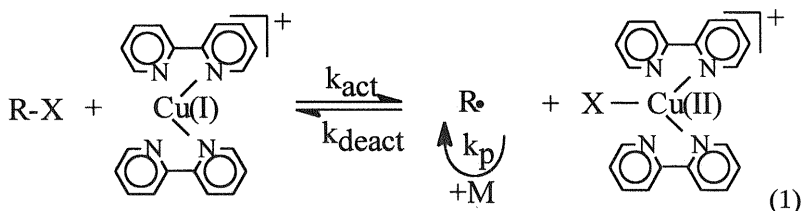
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APPENDIX: LIVING RADICAL POLYMERIZATION

During the preparation of this chapter a new concept of living polymerization based on the reversible stabilization of growing radical by covalent species was reported [1–4]. Although the system needs further optimization, it is worth giving here some of the preliminary findings. So-called atom transfer radical polymerization (ATRP) is analogous to atom transfer addition reactions used in organic synthesis [5] and involves the reversible homolytic cleavage of a carbon–halogen bond by a redox reaction between an organic halide ($R-X$) and transition metal, e.g., copper (I) salts, as illustrated in Eq. (1).



The “living” nature of the process arises from two phenomena: (a) the low stationary concentration of growing radicals and (b) the reversible equilibrium of propagation and deactivation. If the deactivation process does not occur or is very slow, the polymerization becomes a conventional redox-initiated polymerization; transfer and termination reactions may be operative. When one monomer unit is added at each activation in an insertion manner, the process is well controlled. Depending on the catalysts, both heterogeneous and homogeneous polymerizations may be performed with slight differences in polydispersities [6]. For example, heterogeneous systems involving unsubstituted bipyridine as catalyst yield polystyrene with $M_w/M_n = 1.3$, whereas under the same experimental conditions a homogeneous system with 4,4′-di(5-nonyl)-2,2′-bipyridine gives polymers with lower polydispersities ($M_w/M_n = 1.1$). In the case of a heterogeneous system, catalyst concentration is relatively lower and a slower deactivation occurs.

Kinetic studies [7] performed with homogeneous catalysts revealed that the rate of polymerization is first order with respect to monomer and alkyl halide initiator and is usually negative first order with respect to the deactivator and the transition metal complexed by two bipyridine ligands. Kinetics depend on the radical propagation rate constant k_p and the equilibrium constant $K_{\text{eq}} = k_{\text{act}}/k_{\text{deact}}$.

$$R_p = k_{\text{app}}[M] = k_p[P^\cdot][M] = k_p K_{\text{eq}}[\text{In}]_0 \left\{ \frac{[\text{Cu(I)}]}{[\text{XCu(II)}]} \right\} [M] \quad (2)$$

The preceding kinetic equation does not take the “spontaneous formation of the deactivator during polymerization” into account and therefore the actual kinetic law appears to be more complex. ATRP is a multicomponent initiating system and the structure and the concentration of all the components affect the polymerization rate and the properties of the resultant polymers.

Effect of Alkyl Halide

The structure of the alkyl group of the alkyl halide should be similar to that of the monomer for quantitative generation of growing chains [6]. The following alkyl halides resemble the growing chains of the polymerization of the corresponding monomers.

Alkyl halide	Monomer
1-Phenyl ethyl halide	Styrene
2-Halopropionates	Acrylate
2-Halopropionitrile	Acrylonitrile

In general, any alkyl halide with activated-carbon, polyhalogenated compounds and those with a weak halide bonding can be used. Polymeric alkyl halides may also be employed to yield block or graft copolymers. Bromides and chlorides seem to be the most suitable for the purpose. Fluorine is too strongly bound. Iodine is a good leaving group but causes side reactions.

Effect of Transition Metal Salts and Their Ligands

A good catalyst should exhibit high selectivity toward the atom transfer process and participate in a one-electron transfer cycle in order to avoid oxidative addition and reductive elimination reaction resulting from two-electron transfer processes. Moreover, the metal should exhibit low affinity toward the intermediates generated in the process. In general, the ligands have three effects in ATRP processes. They may solubilize the catalytic system, affect the redox chemistry, and control selectivity. In copper, the most active system is one with two bipyridine ligands containing electron-donating substituents such as nonyl groups.

Effect of Deactivators

According to Eq. (1), the Cu(II) complex formed after atom transfer can deactivate the growing radical. The deactivator reduces the rate of polymerization rate and polydispersity of the resulting polymer. In the meantime, deactivator may participate in a side reaction. Therefore, control of the amount and the structure of the deactivator is extremely important.

Effect of the Counteranion

CuPF₆, complexed with two molecules of pyridine, is an efficient system for ATRP of styrene and methyl acrylate [8]. Notably, ligand exchange occurring with mixed systems such as CuBr/R-Cl was not observed due to the noncoordinating nature of CuPF₆. For styrene polymerization employing phenylethylchloride as the alkyl halide, better control of the molecular weight and linear kinetic behavior was observed. The rates of polymerization were enhanced in methyl acrylate polymerization.

Monomers

ATRP is successfully employed in the polymerization of a large variety of vinyl monomers such as styrenes, methacrylates, acrylates, acrylonitrile, and some others [2,9–15]. However, at present, available catalytic systems seem to be unsuitable for the less reactive monomers such as ethylene, olefines, vinyl chloride, and vinyl acetate. In the polymerization of monomers with strong electron-donating groups such as *p*-methoxy styrene, some side reactions arising from the involvement of cationic intermediate are observed. Acrylic and methacrylic acids are also not prone to ATRP because they form Cu(II) carboxylates, which are inefficient deactivators. However, hydroxy derivatives such as hydroxyethyl acrylate and hydroxyethyl methacrylate can be polymerized by ATRP.

Effect of Solvents and Additives

In general, ATRP can be performed in neat monomers [6]. However, solvents with different polarities ranging from benzene to water have been successfully employed. The important factor for the choice of a solvent is the possibility of participation in chain transfer reactions and of interaction with the catalytic system. Notably, the rate of polymerization is reduced in solvent-containing systems.

Temperature and Reaction Time

The rate of polymerization is increased with temperature because of an increase in the propagation rate constant and also an increase in the equilibrium constant [6]. Higher k_p/k_t ratios and better control of the polymerization is achieved at higher temperatures. On the other hand, transfer and some other side reactions become more significant at higher temperatures. Depending on the desired polymer, in relation to functionality, molecular weight, etc., the optimal conditions should be determined for each system.

Application of ATRP in Macromolecular Architecture

The most striking advantage of ATRP is its applicability [16] to the preparation of polymers with complex topologies and compositions which cannot be prepared by other methods or requires multisteps under stringent conditions or the other methods do not yield well defined materials.

Besides homopolymers, statistical, alternating and gradient copolymers can be prepared with ATRP [16–18]. In ATRP all claims have similar amounts of comonomers, whereas in classical free radical polymerization the relative amounts of comonomers vary from chain to chain. Variation in the composition of the comonomers during ATRP results in the variation of the composition of the polymer chain formed. By slowly changing the monomer composition, gradient copolymers can be prepared. This possibility has been demonstrated with methyl acrylate-styrene, methyl methacrylate-styrene, and acrylonitrile-styrene couples. Physical properties of the compositionally uniform gradient polymers are quite different from those of the corresponding block and graft copolymers. These polymers may be used as effective compatibilizers [19].

ATRP has also been applied to block copolymer synthesis [16]. Both sequential monomer addition and two-step procedures were used. The former involves the simple addition of a second monomer to the reaction medium after complete consumption of the first monomer. In the latter case the first monomer, after isolation and purification, was used as macroinitiator for the polymerization of a second monomer in its usual manner. Macroinitiators suitable for ATRP may also be prepared by a polymerization technique other than radical polymerization. This way block copolymers of monomers with different chemical structures are prepared. Such examples include cationic to radical and condensation to radical transformation reactions [20,21].

Polymers obtained by ATRP using bifunctional initiators possess terminal halogen groups that can easily be converted to another functional group. This transformation has been demonstrated by preparing telechelic

styrene with amine end groups. Moreover, by using ATRP and suitable combinations of initiators and monomers, hyperbranched/branched and graft/comb polymers can be prepared [16,22].

In conclusion, although mechanistic details for each individual system still remain to be evaluated before ATRP can be considered as the general route for living radical polymerization, it is certainly a robust polymerization system that can polymerize a wide variety of monomers with a high degree of control. The reaction conditions are not stringent and various macromolecular engineering can be achieved with simple polymerization systems.

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III

TECHNICAL PROCESSES OF VINYL POLYMERIZATION

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11

Continuous Processes for Radical Vinyl Polymerization

Kyu Yong Choi

I. INTRODUCTION

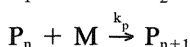
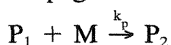
Free-radical polymerization of vinyl monomers takes place through intermediates having an unpaired electron known as free radicals. Many vinyl monomers are readily polymerized by free-radical mechanisms because free-radical polymerization is relatively less sensitive to impurities compared to ionic polymerizations. Free radicals can be generated in a number of ways, including organic or inorganic initiators and even without added initiators (e.g., thermal and photoinitiation). There are over 50 different organic peroxides and azo initiators in over 100 different formulations produced commercially. Initiators are selected based on several factors: polymerization rate, reaction temperature, solubility, and polymer properties.

A typical-free radical homopolymerization process consists of the following reactions:

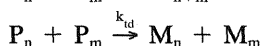
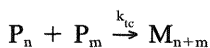
Initiation



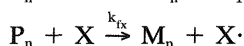
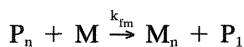
Propagation



Chain termination



Chain transfer



In the above, M is the monomer, I is the initiator, R is the primary radical, P_n is the live polymer radical with n monomer repeat units, M_n is the dead polymer with the n monomer repeat units, and X is the solvent, impurity, or chain transfer agent. At high monomer conversion, the polymer's mobility decreases and termination reactions become diffusion controlled ("gel effect"). As a result, the polymerization rate increases rapidly and the polymer's molecular-weight distribution becomes broad.

Commercial free-radical polymerization processes are subdivided into bulk (mass), solution, suspension, emulsion, dispersion, and precipitation polymerization. In bulk polymerization, where no solvent is present, polymers may be soluble in their own monomers [e.g., polystyrene, poly(methyl methacrylate), poly(vinyl acetate)] or insoluble in their monomers [e.g., poly(vinyl chloride), polyacrylonitrile]. Although pure polymers are obtainable, high viscosity with an increasing monomer conversion limits the maximum solid content in the reactor. In solution polymerization, solvent miscible with a monomer dissolves the polymer (e.g., styrene in ethyl benzene) and the viscosity of a polymerizing solution is relatively low and the polymerization takes place homogeneously. In suspension polymerization, the organic monomer phase is dispersed as small droplets by mechanical agitation and polymerized to hard solid polymer particles with monomer-soluble initiators. Each monomer droplet acts like a single microbatch polymerization reactor. The polymer particle size or its distribution is governed by mechanical agitation and surface stabilizer. Emulsion polymerization differs from suspension polymerization in two important respects: The initiator (water soluble) is located in the aqueous phase, and the polymer particles produced are typically of the order of 0.1μ in diameter, about 10 times smaller than the smallest encountered in suspension or dispersion polymerization. The use of water in both suspension and emulsion polymerization reactors facilitates the removal of polymerization heat.

A variety of polymerization reactors are used in industrial polymerization processes. They are, for example, continuous reactors, semibatch reactors, and batch reactors. The choice of reactor type or configuration for a given polymerization reaction depends on many factors such as polymerization mechanism, thermodynamic properties of monomers and polymerizing fluid, production rate, reaction conditions (e.g., temperature, pressure, viscosity, phases, etc.), heat removal capacity, product properties, investment and operating cost, operability, and controllability. Whereas batch reactors are useful for small-to-intermediate volume polymers or specialty polymers, continuous reactors are suitable for a large-scale production of commodity vinyl polymers such as polystyrene, poly(methyl methacrylate), poly(vinyl acetate), and polyethylene. Compared to batch reactors, in which batch-to-batch variations in product quality can be a problem, continuous reactors have advantages in that polymer quality control through process automation can be achieved more effectively. For example, in a batch copolymerization reactor, a composition drift occurs because monomers have different reactivities. In a continuous reactor operating at steady state, all polymer molecules are made under the same reaction condition, and, thus, compositional heterogeneity can be prevented.

In continuous industrial free-radical polymerization processes, many different types of reactors are used [1]. They are continuous-flow stirred tank reactors, tower reactors, horizontal linear flow reactors, tubular reactors, and screw reactors. In some processes, different types of reactors are used together in a reactor train. In stirred tank reactors, no spatial concentration and temperature gradients exist, whereas in linear flow or tubular reactors, concentration and temperature vary in the direction of flow of the reacting fluid. Specially designed reactors such as screw reactors or extruder reactors are also used to produce specialty vinyl polymers. In this chapter, some important characteristics of continuous reactors used in industrial free-radical polymerization processes are discussed.

II. CONTINUOUS POLYMERIZATION REACTORS FOR FREE-RADICAL POLYMERIZATION OF VINYL MONOMERS

A. Continuous Stirred Tank Reactors

Continuous stirred tank reactors (CSTRs) are perhaps the most widely used in industrial continuous free-radical polymerization processes. Monomers, solvents, initiators, and additives (e.g., chain transfer agents) are continuously fed to a mechanically agitated reactor and the product solution is removed continuously from the reactor. In a CSTR, the reaction mixture is

backmixed by a mechanical stirrer and its effluent temperature and composition are the same as the reactor contents if perfect backmixing is achieved in the reactor. The liquid level is normally held constant by controlling the product withdrawal rate. At steady state, the polymerization rate and polymer properties are time-invariant; thus, uniform quality product is obtainable. However, some variations in the reaction conditions should also be expected [e.g., feed purity, feed temperature, cooling water source temperature (seasonal variations), etc.]; thus, it is required to have an efficient closed-loop control system to regulate such variations and to keep the reactor at its target operating conditions. In a large continuous stirred tank reactor, varying degrees of imperfect mixing (e.g., segregation, short circuiting, and stagnation) or temperature nonuniformity may exist in the reactor. In such a case, some inconsistency in the product properties may result. Because the mixing is provided by mechanical agitation, stirred tank reactors are suitable for relatively low-viscosity fluids. For high-viscosity fluids, specially designed reactors and agitators (e.g., helical ribbons, anchors, scroll agitators) are required for efficient mixing and heat transfer.

In industrial polymerization processes, multiple CSTRs are also commonly used. Each reactor is operated at different reaction conditions to achieve desired final polymer properties. In a typical CSTR polymerization system, the reaction heat is removed through a jacket in which cooling fluid is circulated. To provide an additional heat removal capacity, internal cooling coils, external heat exchanger, and reflux condensor may be installed.

Continuous stirred tank reactors are used commercially for solution, bulk (mass), and emulsion polymerization of vinyl monomers. In bulk homogeneous polymerization processes (e.g., polystyrene), the reactor system usually consists of a single CSTR or multiple CSTRs and an extruder-type devolatilizer to remove unreacted monomer, which is then recycled to the reactor. As monomer conversion increases, the viscosity of the polymerizing fluid increases and the overall heat removal efficiency decreases. When styrene is polymerized in bulk in a stirred tank reactor, monomer conversion is limited to about 30–40% due to an increasing viscosity of the polymerizing fluid above this conversion level. However, the overall monomer conversion can be very high because unreacted monomer is constantly recycled to the reactor.

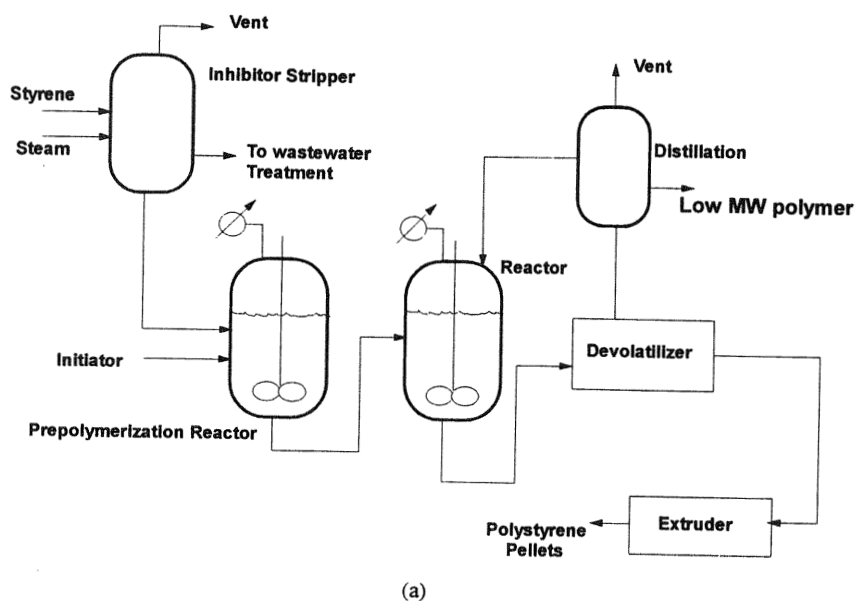
Figure 1 shows some examples of continuous stirred tank reactor systems for free-radical vinyl polymerization processes. In the bulk styrene polymerization process shown in Fig. 1a [2], styrene monomer, stripped of inhibitor added for transportation, is supplied to a prepolymerization reactor with an organic initiator. The monomer–polymer mixture is then fed to a series of stirred tank reactors operating at higher temperatures than in the prepolymerization reactor. At low temperatures, the polymer's molecular

weight is high, and as the reaction temperature is increased, molecular weight decreases. The unreacted monomer and low-molecular-weight polymers or oligomers are removed in a devolatilizer. The volatile monomer is then distilled off and recycled to the polymerization reactor. The purified polymer is pelletized in an extruder. Although only two CSTRs are shown in Fig. 1a, more than two CSTRs can be used. Instead of stirred tank reactors, tower reactors can also be combined in a reactor train with CSTRs. When a series of CSTRs or tower reactors are used, the polymerization temperature is progressively raised through the reaction zone to deal with a polymeric fluid of increasing viscosity.

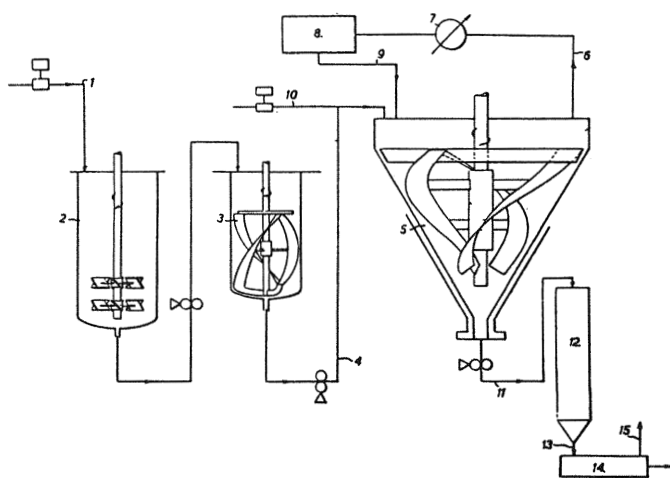
A cascade of polymerization reactors is used for the production of high-impact polystyrene (HIPS). Impact polystyrene is a polymer toughened by a rubber within the polystyrene matrix. A continuous reactor system for mass polymerization of styrene with polybutadiene rubber is illustrated in Fig. 1b [1]. In the first reactor agitated by a turbine impeller, the conversion of styrene is maintained at about 8%, which is slightly ahead of the phase-inversion point. The second reactor is fitted with a scroll agitator and conversion is increased to about 23%. The first two reactors are used to avoid problems with rubber-phase particle size and gel formation due to excessive backmixing of the reaction mixture near the phase-inversion point. The polymerization is continued in the third reactor operating at 173°C and 86% conversion with a 2.4-hr residence time. This reactor is cooled by a refluxing styrene monomer. Finally, the reaction is completed in an unagitated tower reactor to about 97% conversion at 207°C.

In the polymerization process shown in Fig. 1c [3], a fresh feed of 8% polybutadiene rubber in styrene is added with antioxidant and recycled monomer to the first reactor operating at 124°C and about 18% conversion at about 40% fillage. The agitator is a horizontal shaft on which a set of paddles is mounted. Because the temperature in each compartment can be varied, it is claimed that the linear flow behavior provided by the reactor staging results in more favorable rubber-phase morphology than would be the case if the second reactor were operated as a single continuous stirred tank reactor.

In operating a continuous stirred tank reactor, maintaining a desired polymerization temperature is often the most important objective. It is because the polymerization rate and many of the polymer properties are strongly dependent on temperature. For example, polymer molecular weight decreases as the reaction temperature is increased. If the reaction heat is not properly removed, excessive pressure buildup and/or thermal runaway may occur. In a jacketed reactor, the removal of reaction heat becomes increasingly difficult as the reactor volume increases because of the reduced heat transfer area/reactor volume ratio. Table 1 illustrates the jacket surface areas



(a)



(b)

Figure 1 Examples of continuous stirred tank reactors for free radical polymerization.

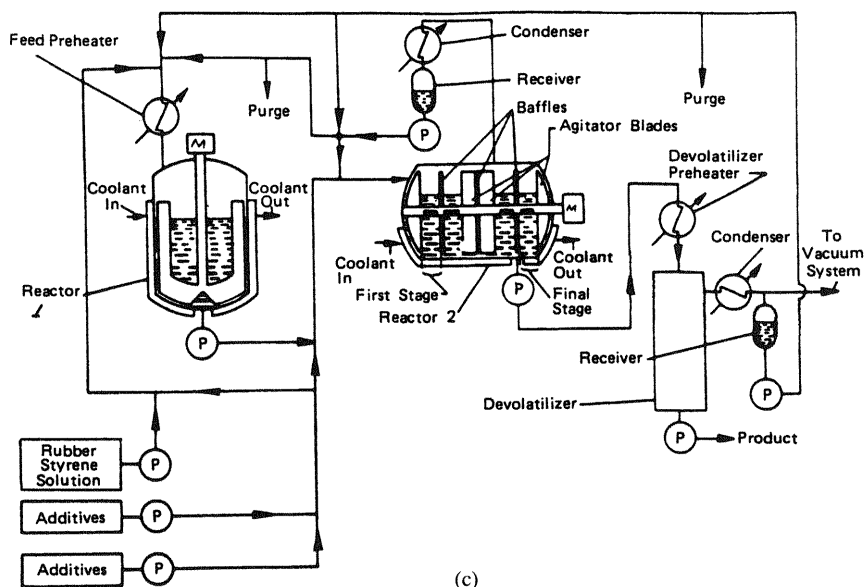


Figure 1 (continued)

of agitated polymerization reactors. Large polymerization reactors require, in addition to a cooling jacket, the installation of internal cooling baffles or internal cooling coils and, frequently, of reflux condensers.

When continuous stirred tank reactors are used for polymerization, less than 100% conversion is usually obtained. Thus, a large quantity of unreacted monomers and solvent are separated from the polymerizing mixture, purified, and recycled to the reactor. Continuous reactors are also useful in

Table 1 Jacket Surface Areas of Agitated Polymerization Reactors

Reactor volume (U.S. gal)	Cooling area (ft ²)
2,000	180
3,000	245
3,700	292
6,300	392
16,500	744

Source: Ref. 4.

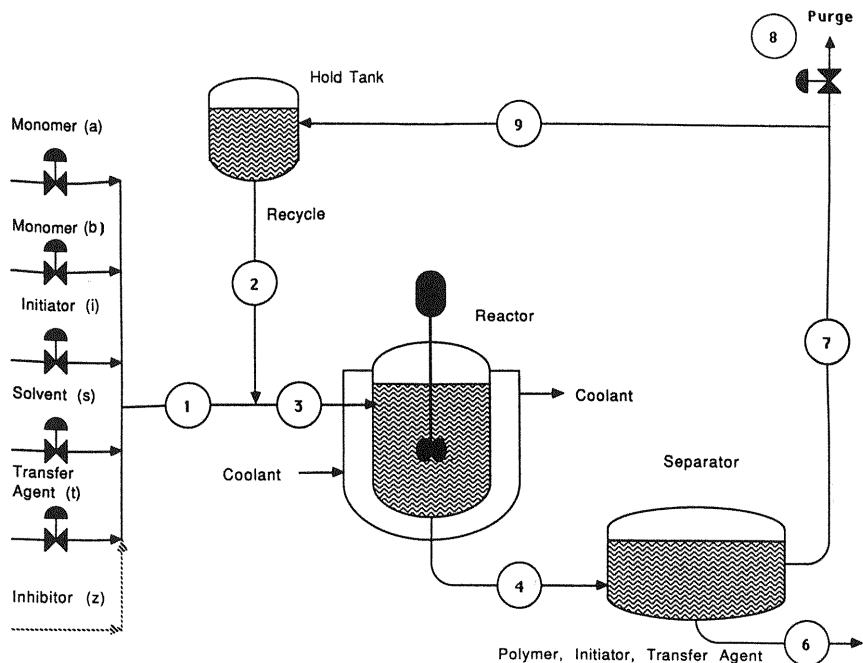


Figure 2 Continuous copolymerization reactor with recycle.

manufacturing copolymers. Figure 2 illustrates a schematic of a continuous copolymerization reactor with recycle [5]. Here, two monomers (methyl methacrylate and vinyl acetate) and an initiator are supplied to the reactor with solvent and chain transfer agent. In this process where both polymer molecular weight and copolymer composition are controlled, the process disturbances (e.g., impurities, compositional variations) caused by the recycle stream must be properly regulated to ensure consistent copolymer quality. To do so, an advanced multivariable control technique can be applied to minimize process interactions and disturbances [5].

B. Multizone Stirred Reactors

Multizone stirred reactors have been used for the polymerization of ethylene to low-density polyethylene (LDPE) and for the polymerization of styrene and its comonomers. In general, the reactor is a vertical or a horizontal vessel of a large length/diameter ratio. The reactor is divided into several equal or nonequal volume internal compartments, and reactor internals are designed

to provide good radial mixing but also some axial segregation. Thus, the flow and mixing characteristics of the multizone reactors are somewhere between those of a single stirred tank reactor and a plug flow reactor (e.g., tubular reactor) and they are sometimes called as linear flow reactors (LFRs). The main motivation for using the multizone reactors is that the polymerization conditions (e.g., temperature and composition) can be widely varied along the length of the reactor to obtain desired polymer yield and polymer properties. For example, comonomers or other reactive additives can be injected in different concentrations to each compartment. In designing and operating tower reactors or linear flow reactors, it is important to ensure uniform radial mixing in the reactor vessel. If any radial velocity gradients are present, a buildup of a high-viscosity polymer layer may occur, lowering the heat transfer efficiency. Because any changes in the upstream reactor or reaction zones affect the performance of the downstream reactors, it is also important to design reactor control systems that will offset any process upsets. Thus, the design and operation of the reactor becomes more complicated than using a single-zone stirred tank reactor.

1. Polyethylene Reactors

Low-density polyethylene (density = $0.915\text{--}0.935\text{ g cm}^{-3}$) has long been manufactured by free-radical polymerization using continuous autoclave reactors. The autoclave reactor shown schematically in Fig. 3a is a typical multizone ethylene polymerization reactor. The reactor is typically a vertical cylindrical vessel with a large L/D ratio. The reacting fluid is intensely mixed

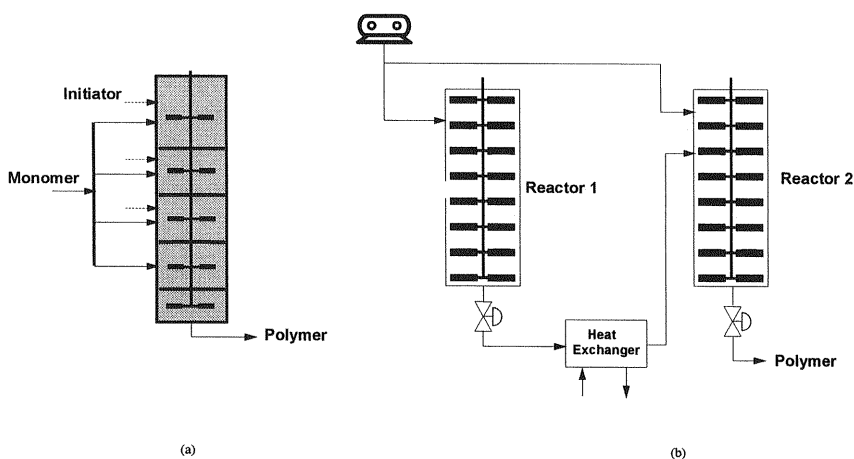


Figure 3 Multizone reactors for high-pressure ethylene polymerization.

by an agitator which consists of a vertical shaft to which impeller blades are attached to ensure efficient mixing of monomers, polymers, and initiators. High-pressure ethylene is supplied to each reaction compartment with a peroxide initiator. Depending on the polymer properties desired, the feed rates of ethylene and initiator to each reaction zone are varied. Because the polymerization occurs at high pressure (1500–2000 atm), the reactor wall thickness is large; thus, the reactor is operated adiabatically. The heat of polymerization ($21.2 \text{ kcal mol}^{-1}$) is removed by the bulk flow of the polymerizing fluid. In general, the feed ethylene temperature is substantially lower than the reactor temperature. The polymerization temperature in each zone is controlled by regulating the initiator injection rate. Cold monomer feeds may be added to a few selected reaction compartments to remove additional reaction heat. As the polymerization rate is very high, the reactor residence time is very short (e.g., 1–3 min). In high-pressure ethylene polymerization, polymer properties (e.g., molecular weight, molecular-weight distribution, short-chain and long-chain branching frequencies, etc.) are strongly affected by polymerization temperature, pressure, and initiator type. More than one autoclave reactor can also be used for LDPE production. In the polymerization process shown in Fig. 3b [6], the reaction mixture of about 15% ethylene conversion is cooled by a heat exchanger placed between the two autoclave reactors. Because additional reaction heat is removed by the external heat exchanger, a higher ethylene conversion (25%) has been claimed to be obtainable. Similar multiple reactor configurations are also reported in patent literature [7]. In ethylene polymerization processes, a loss of uniform mixing or the presence of impurities in the reacting fluid may cause a rapid decomposition of ethylene and polyethylene. Therefore, it is crucial to maintain perfect backmixing in each reaction zone. Strong nonlinear behavior of high-pressure autoclave reactors and the effect of micromixing have been the subject of research by some workers [8–11].

2. Tower Reactors for Styrene Polymerization

The tower reactors similar to the ethylene polymerization reactors are used in other free-radical vinyl polymerization processes. Figure 4a shows a schematic of the tower reactor for bulk styrene polymerization developed by Farben in the 1930s [4]. The prepolymers prepared in batch prepolymerization reactors to about 33–35% conversion are transferred to a tower reactor whose temperature profile is controlled from 100°C to 200°C by jackets and internal cooling coils. There is no agitation device in the tower reactor. The product is then discharged from the bottom of the tower by an extruder, cooled, and pelletized.

Figure 4b also shows a continuous bulk styrene polymerization reactor system which consists of a series of towers using slow agitation and grids of pipes through which a mixture of diphenyl oxide is circulated for temperature control [4]. In this reactor system, each reactor is mildly stirred and operating at different temperatures. Ethyl benzene (5–25%) may be added to a styrene feed stream to reduce the viscosity of a polymer solution and to ease heat transfer. A vacuum degasser removes the residual styrene and ethylbenzene, which are recycled to the first reactor.

In a multizone reactor for the manufacture of impact polystyrene as illustrated in Fig. 4c [12], a portion of product stream is cooled in an external heat exchanger and recycled to the top of the reactor. At a high recirculation rate, mixing is between backmixed and plug flow. In this reactor, horizontal rod agitators or layers of tubes are installed at each level to create shearing action throughout the mass of rubber–styrene solution undergoing polymerization [13]. This reactor is called the recirculated stratified agitated tower. Figure 4d shows a stratifying polymerization reactor patented by Dow Chemical Co. [14]. In this reactor, the revolving rods prevent channeling and promote plug flow.

3. Horizontal Linear Flow Reactors

Another type of linear flow reactor system for the synthesis of high-impact polystyrene is shown in Fig. 5 [1]. Here, the first-stage backmixed reactor (CSTR) is maintained just beyond the phase-inversion point (98°C, 14% solids) and the dissolved styrene reacts to form either a graft copolymer with the rubber or a homopolymer in the linear flow reactor train. Note that a portion of the effluent (130°C, 35% solids) from the second reactor is recycled to the first reactor. The temperature of the polymerizing mixture is gradually increased as it travels through the linear flow reactors and the final conversion of about 72% is achieved.

4. Continuous Suspension Polymerization Reactors

Suspension polymerization of vinyl monomers is usually carried out in batch reactors. However, the feasibility of continuous suspension polymerization has been reported in some literature. A multiple-reactor system for continuous suspension polymerization of vinyl chloride is illustrated in Fig. 6 [15]. Monomer, water, initiator, and suspending agents are fed to a vertical tower reactor equipped with a multistage stirrer. The reaction mixture of about 10% conversion is then transferred to the second and third reactors, which contain blade stirrers. Each reactor is jacketed for heat removal. Plug flow of the polymerization mixture is maintained in the reaction zones.

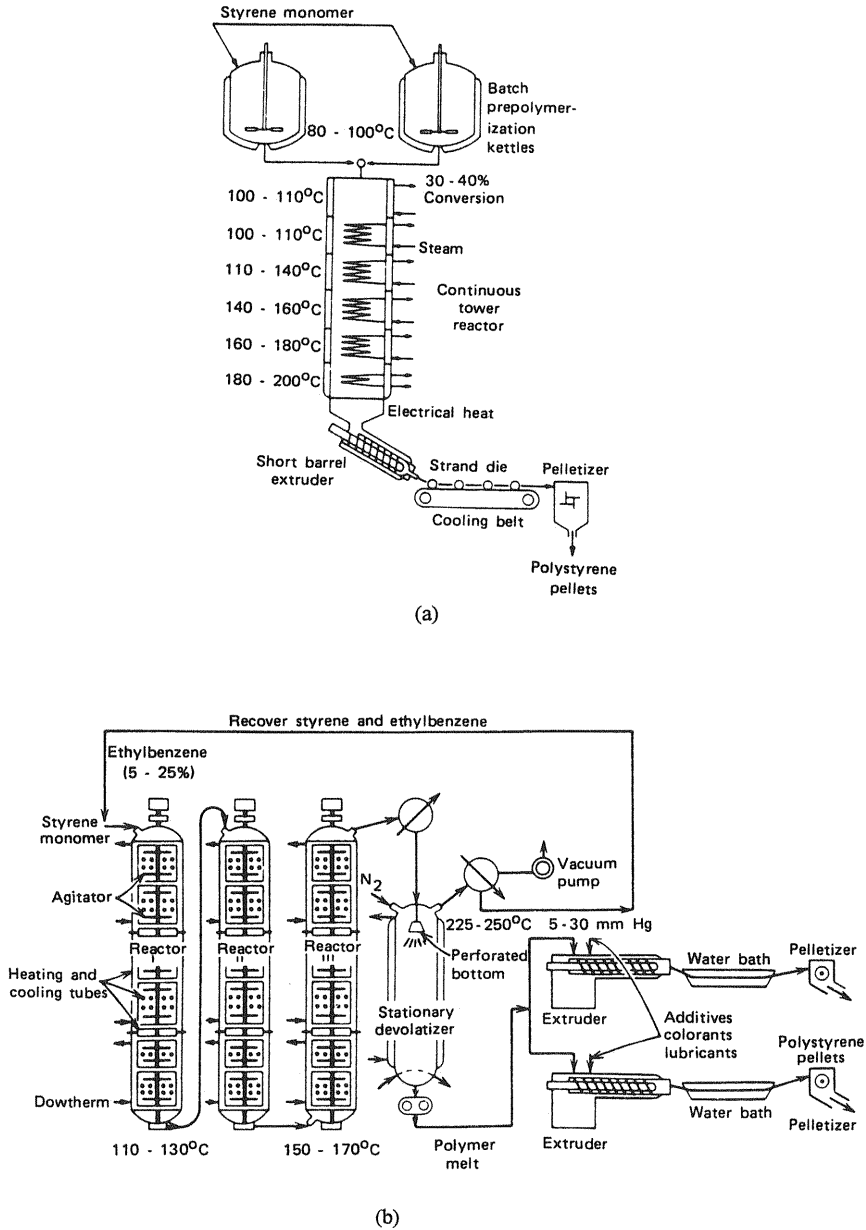
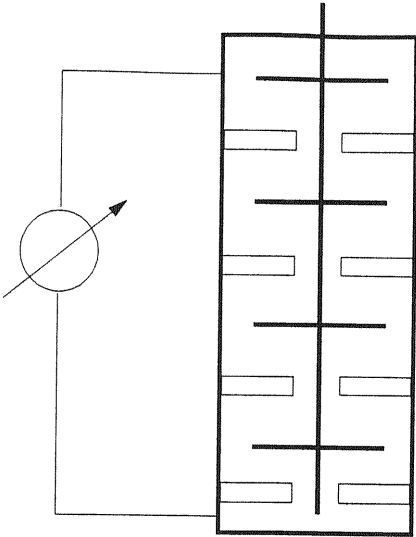
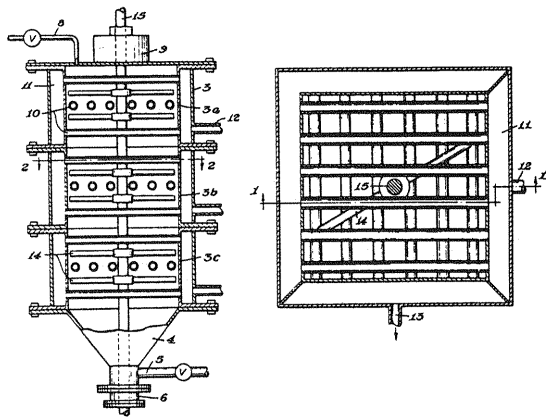


Figure 4 Tower reactors for styrene bulk polymerization.



(c)



(d)

Figure 4 (continued)

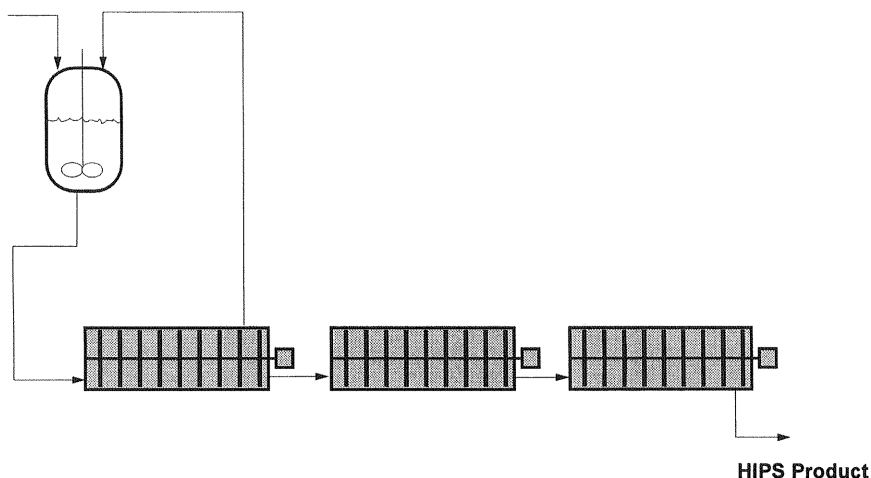


Figure 5 Continuous reactor system for mass polymerization of high-impact polystyrene.

5. Continuous Emulsion Polymerization Reactors

Emulsion polymers (latex) have long been produced by continuous processes due to the low viscosity of latex polymers. Certain emulsion polymerization systems (e.g., polyvinyl chloride, polyvinylacetate) often exhibit large and sustained oscillations in conversion and polymer and latex properties such as number of particles, particle size, and molecular weight. Figure 7a illustrates the conversion and number of polymer particles versus reactor residence time for a single CSTR. Such oscillatory behaviors are due to the periodic formation and depletion of soap micelles, which lead to short periods of rapid particle generation followed by long periods in which no nucleation occurs. Because the polymer particles are not covered adequately by soap, particle agglomeration occurs during the periods of rapid particle nucleation. This problem can be solved by reconfiguring the process system. For example, a very small seeding reactor precedes the main polymerization reactor, as shown in Fig. 7b. Only a portion of the monomer and water are fed to the seeding reactor, and the remainder is fed to the main reactor. Then, particle generation is complete in the seeding reactor by using high soap and initiator concentrations. Only particle growth occurs in the main reactor. Figure 7c shows the resulting monomer conversion and the number of polymer particles versus reactor residence time [16]. This example illustrates that the understanding of polymerization mechanism and kinetics is crucial in designing efficient continuous polymerization reactor systems.

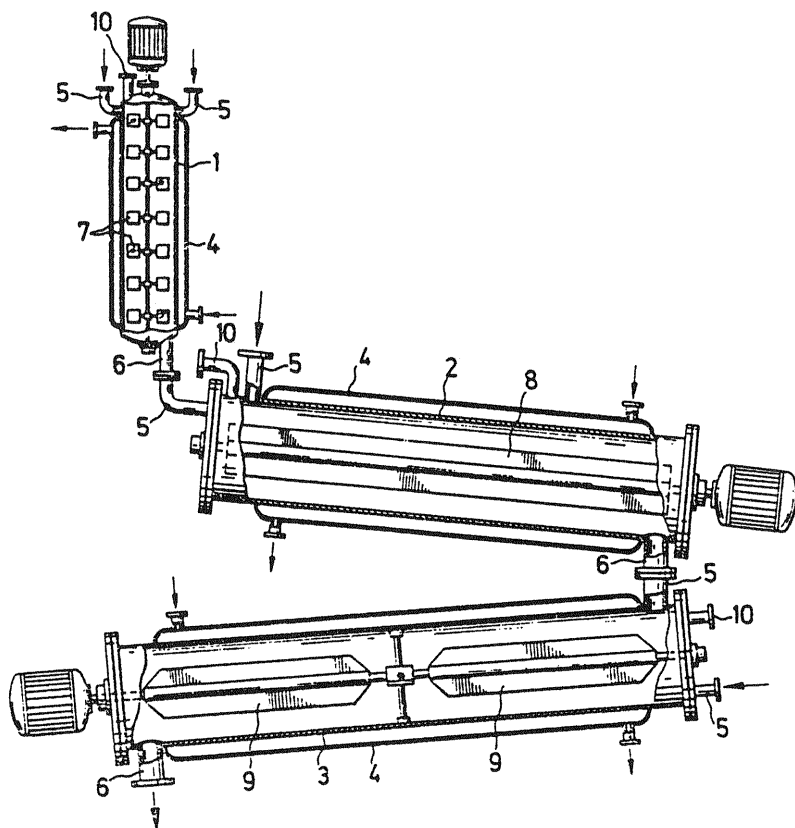
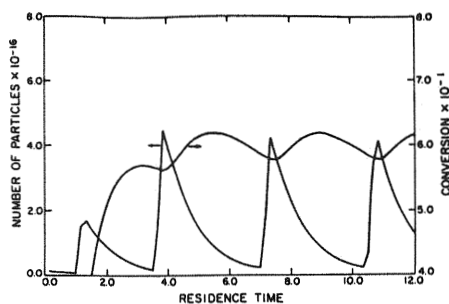


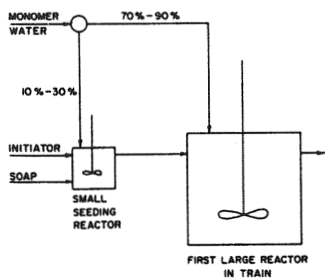
Figure 6 Continuous suspension polymerization reactor for vinyl chloride.

C. Tubular Reactors

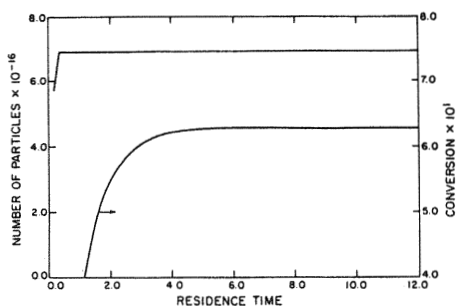
Vinyl monomers can be polymerized in tubular reactors. The main difference between tubular reactors and stirred tank reactors is that backmixing of the reactor's content is minimal in the tubular reactor. Tubular reactors have certain advantages over stirred tank reactors: design simplicity, good heat transfer capability, and narrow molecular-weight distribution of the product polymer due to minimal backmixing. The large surface area/volume ratio is particularly advantageous for the dissipation of heat generated by exothermic polymerization. However, empty tubular reactors are not widely used for commercial production of vinyl polymers except for high-pressure ethylene polymerization. One of the major problems in using the empty tubular reactors for the polymerization of vinyl monomers is that the viscosity of the



(a)



(b)



(c)

Figure 7 Continuous emulsion polymerization (a) conversion and number of particles vs. residence time for a single CSTR; (b) reactor system with a small seeding reactor; (c) conversion and number of particles vs. time with a seeding reactor.

polymerizing fluid increases significantly as monomer conversion increases. As a result, large radial and axial temperature gradients may exist and the velocity profile is significantly distorted. Then, a buildup of a slowly moving liquid layer occurs at the reactor walls, causing a large variation in residence time distribution, plugging problems, poor heat transfer, and poor product quality [17]. These phenomena have been the subject of extensive theoretical modeling and experimental studies [18–20]. To minimize the radial velocity gradient, internal mixing elements such as paddles or static mixers can be installed in the tubes [21,22]. Recently, a 30,000-ton/year polystyrene plant has been constructed using static mixer reactors (Fig. 8) [23]. In the first polymerization stage, monomer and solvent are fed to the recirculating loop reactor, consisting of SMR static mixer–reactors. This reactor consists of bundles of intersecting tubes through which the heat transfer medium flows. In addition to the radial mixing of the product stream at low shear rate, high heat transfer coefficients are obtained, and a large internal heat transfer surface is formed by the tubes. As a result, relatively small temperature gradients exist in the reactor. The reaction temperature and polymerization rate are controlled via the temperature of the heat transfer fluid flowing through the tube bundles of the static mixer–reactors. In the second polymerization stage, the monomer/polymer solution flows to the plug flow reactors filled with static mixers. In these reactors, the monomer/polymer solution is radially mixed to such an extent that temperature, concentration, and velocity over the reactor cross section are kept nearly constant. The polymerization temperature is increased gradually, resulting in increased conversion. It has been claimed that the uniform molecular weight of the final polymer is the result of a well-controlled time–temperature history.

1. High-Pressure Ethylene Polymerization Reactors

The most well-known tubular polymerization reactor system is the one used in high-pressure ethylene polymerization processes for the production of low-density polyethylene. Figure 9 shows a classical high-pressure, high-temperature tubular ethylene polymerization reactor system. The reactor can be either a long single tube, a tube with multiple feed streams along its length, or a bundle of tubes, mounted vertically or horizontally. To provide plug flow, a high length-to-diameter ratio (250/1 to 12,000/1) is employed. Purified ethylene is compressed to 1000–3500 atm and mixed with a free-radical initiator (oxygen) and the residence time is as low as 20 sec. The first section of the tubular reactor is heated because the heat generated by polymerization is insufficient. The second section of the reactor is cooled to provide the desired temperature profile. Because the fluid velocity is very high, a pressure drop along the tube length is significant and it affects the

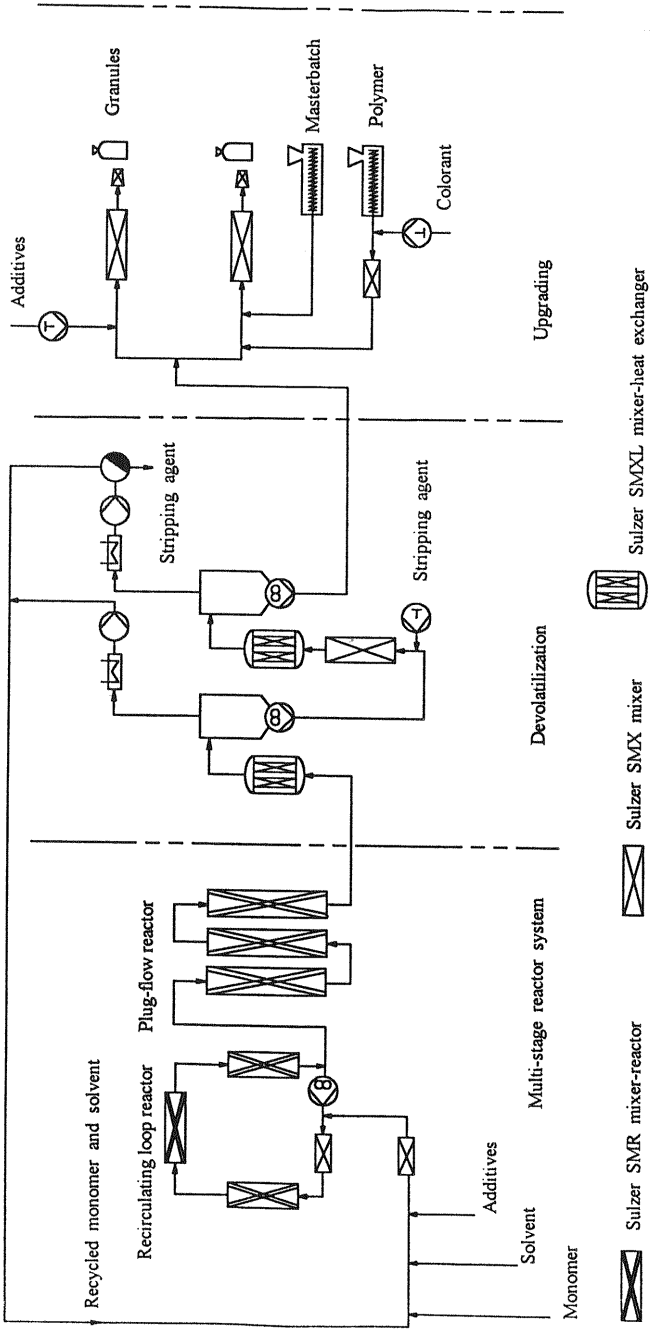


Figure 8 Schematic flow sheet of the bulk polystyrene process with static mixers.

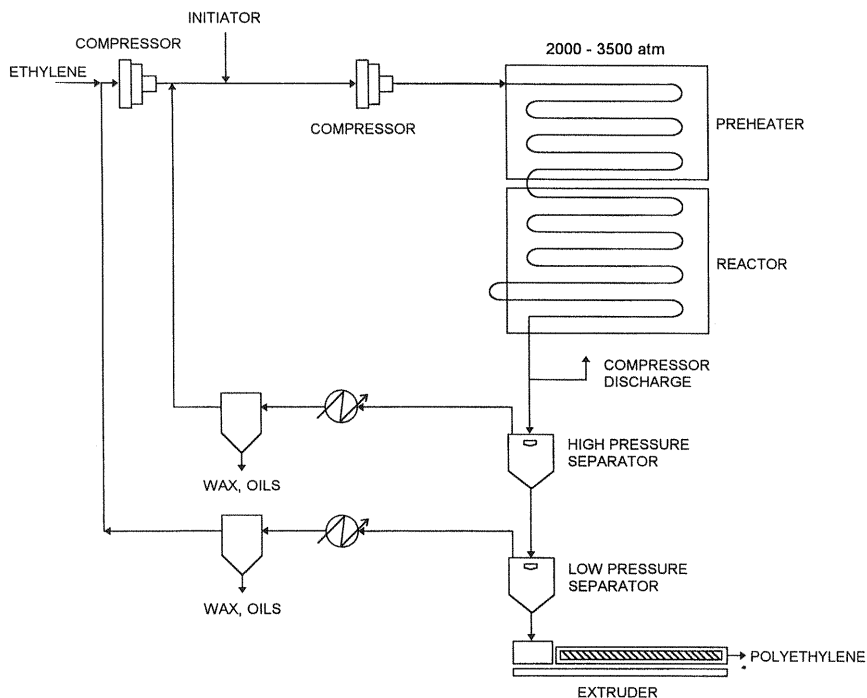


Figure 9 A tubular reactor system for free-radical ethylene polymerization.

propagation rate. As a result, polymer's molecular-weight distribution is broader than by using a stirred autoclave reactor [4]. Chain transfer agents such as ketones, aldehydes, alcohols, hydrogen, or chlorinated compounds are added to narrow molecular-weight distribution. The reaction product is discharged into high and low pressure separators.

2. Continuous Tubular Suspension Polymerization Reactors

Suspension polymerization is mostly carried out in batch reactors. However, there are some reports on the continuous suspension polymerization in different types of reactors. For continuous suspension polymerization, there are certain requirements: (a) narrow residence time distribution to achieve high conversion, (b) good mixing of the two phases to obtain polymers with proper particle size distribution, (c) no dead space and gas phase within the reactor to avoid reactor fouling, and (d) large heat transfer surface area for

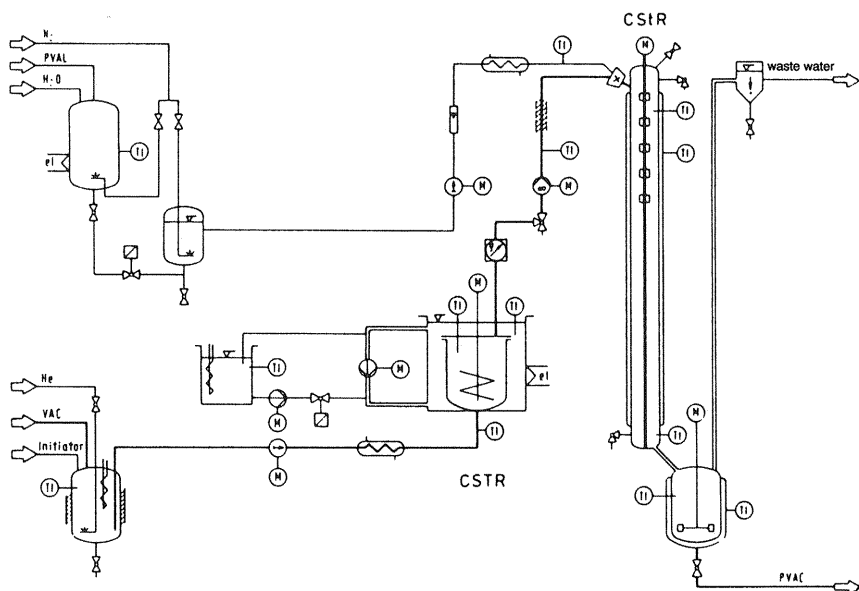


Figure 10 Flow diagram of a continuous suspension polymerization reactor system.

heat removal. Figure 10 shows a schematic of a pilot plant-scale continuous suspension polymerization reactor system [24]. The reactor consists of a tube with a blade stirrer. Vinyl acetate containing organic initiator, and a water-containing dispersion agent are pumped in parallel flow through the tube reactor from top to bottom. The conversion was obtained above 90%, and good particle size distribution was obtained.

3. Tubular Emulsion Polymerization Reactors

Because a tubular reactor offers minimal backmixing, it can produce latex polymers with a narrow particle size distribution. There is a large amount of literature on emulsion polymerization in tubular reactors (nonagitated and agitated) [25–27]. One of the major problems in operating a tubular reactor for high conversion emulsion polymerization is the occurrence of fouling and plugging. In a recent study, it has been shown that the use of a pulsation source can eliminate the reactor fouling and plugging problems in a laboratory-scale tubular emulsion polymerization reactor to obtain a narrow particle size distribution at high monomer conversion [28,29].

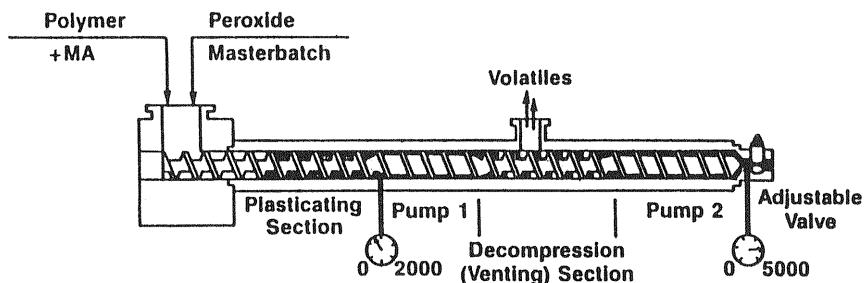


Figure 11 Extruder reactor for the grafting of maleic anhydride.

D. Continuous Screw Reactors

Twin-screw extruders have long been used by the plastic compounding industry for mixing and dispersing of one or more components into a polymer matrix. Because twin-screw extruders provide the excellent control of mixing characteristics and gas, liquid, or solid feed can be added at any point along the extruder length, they are also used to produce high-performance specialty polymers. The batch size versatility of extruders compared to full-scale polymerization reactor is particularly attractive for the manufacture of specialty polymeric materials. In the reactive extrusion process, the appropriate monomer(s), prepolymers, and initiator(s) are fed to an extruder where the polymerization takes place, and the resulting polymer is forced into a mold or a die to give a finished article. Figure 11 illustrates a two-stage extruder reactor for the grafting of maleic anhydride onto polyolefins [30]. In the first stage, unreacted maleic anhydride is vented, and in the second stage, the reaction mixture is pressurized to the die. The feeds to the reactor consist of a peroxide master batch and the feedstock to be grafted. As the polymer feeds are being melted and mixed, the temperature rises with distance down the reactor.

III. DESIGN AND OPERATION OF CONTINUOUS FREE-RADICAL POLYMERIZATION REACTORS

At steady state, continuous polymerization reactors produce the polymers of constant properties. In reality, however, the reactor is subject to some external disturbances such as variations in feed composition, feed temperature, and cooling water source temperature. Therefore, accurate feedback control of the reactor is required to maintain consistent product quality and reactor

stability. When several different-grade products are manufactured, the reactor conditions must be changed for each grade.

It is also known that continuous polymerization reactors may exhibit highly nonlinear dynamics such as multiple steady states, autonomous oscillations, and strong parametric sensitivity. Thus, it is important to understand the steady state and dynamic behaviors of a reactor in order to maintain reactor stability and to achieve smooth transitions for grade changes.

As described earlier, the control of polymerization temperature is often the most important objective in operating a polymerization reactor. In Fig. 12, three commonly used configurations for heat removal in continuous stirred tank reactors are illustrated [31]. In the jacketed reactor (Fig. 12a), temperature is controlled by both internal cooling coils and a jacket. The jacket temperature is regulated in response to the reactor temperature. For a large reactor vessel, some time delays may be present between the jacket temperature and the resulting reactor temperature, causing a potential temperature instability. Figure 12b shows the autorefrigerated reactor in which controlled vaporization of the monomer and solvent serves to remove the heat of polymerization. The reactor temperature and pressure are maintained very close to the bubble point. Figure 12c shows a temperature control

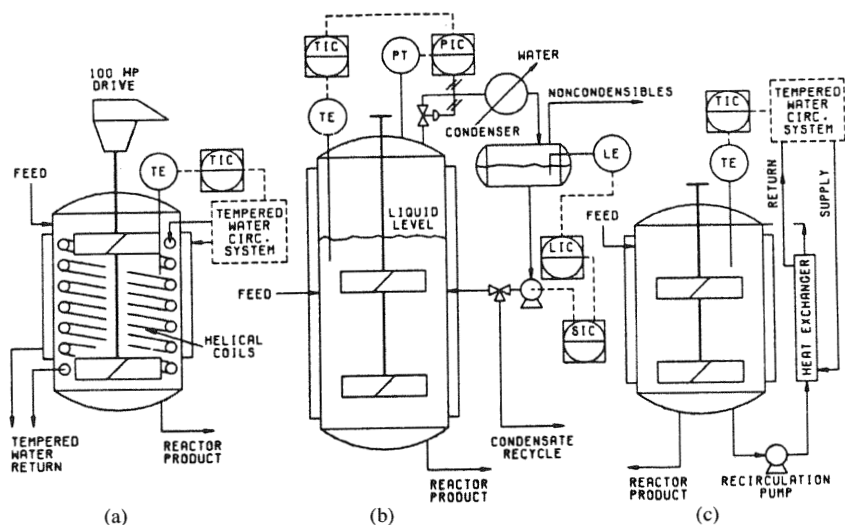


Figure 12 Polymerization reactor temperature control schemes. (a) temperature control via cooling jacket and coils; (b) temperature control via vaporization of solvent/monomer; (c) temperature control via forced circulation of syrup through external heat exchanger.

scheme for the reactor with an external heat exchanger. A buildup of high-viscosity polymer layers on the low-temperature heat exchanger surfaces can lower the heat transfer efficiency.

The design of reactor control system is an integral part of the polymerization process design. Some important problems and needs in designing effective controls for industrial polymerization processes are (i) on-line measurements, (ii) severely nonlinear processes, (iii) modeling and identification for control system design, (iv) modeling for simulation and operator training, and (v) process monitoring and diagnosis [32]. Some commercial software packages are available for the modeling of a variety of continuous free-radical polymerization processes.

In industrial continuous polymerization processes, it is often required to produce the polymers of different properties. Obviously, certain reaction parameters must be changed. If the reactor residence time is large (e.g., several hours), it becomes crucial to bring the reactor from one steady-state operating condition to a new steady-state condition as rapidly as possible to minimize the production of transition products. In general, process variables such as temperature, pressure, and bulk phase composition change much faster than those related to polymer properties (e.g., polymer molecular weight, molecular-weight distribution, copolymer composition, morphology, etc.). Unfortunately, these polymer properties are difficult to monitor on-line and they are usually measured infrequently by off-line laboratory analysis. Because continuous polymerization reactors produce a large quantity of polymer products, such time delays in property measurement may cause a significant loss of productivity. To solve such problems, advanced state estimation techniques have recently been developed [33–36]. For example, a dynamic process model (first-principles model based on mass and energy balances) is used on-line in conjunction with a state estimator such as an extended Kalman filter to calculate the polymer properties (e.g., molecular-weight averages, copolymer composition, particle size distribution, etc.) with infrequent process measurements with some time delays. Then, the predicted or estimated polymer properties are used to regulate reactor control variables and to keep the reactor at its target operating conditions.

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12

Technical Processes for Industrial Production

Kyu Yong Choi, Byung-Gu Kwag, Seung Young Park, and
Cheol Hoon Cheong

I. INTRODUCTION

Polymerization of vinyl monomers is of enormous industrial importance. These vinyl polymers are mostly thermoplastics and they are used in a wide variety of end-use applications. Many vinyl monomers are polymerized by free-radical, ionic, and coordination polymerization mechanisms. Among these, free-radical polymerization is the most widely used in industrial production of vinyl polymers. Ionic polymerization is generally used to manufacture specialty polymers. Free-radical polymerization is advantageous over other processes in that it is less sensitive to impurities in the raw materials, and the rate of polymerization as well as polymer properties can be controlled by the choice of initiator and polymerization conditions.

In the homopolymers of vinyl or olefinic monomers, polymer architecture represented by molecular-weight distribution, molecular-weight averages, and long-chain and short-chain branching has a significant impact on the physical, mechanical, and rheological properties of polymers. These properties are strongly influenced by specific polymerization process conditions. The properties of vinyl polymers are also varied widely by copolymerizing two or more vinyl monomers or diens.

One common factor in most of the free-radical polymerization processes is that polymerization reactions are highly exothermic and the vis-

cosity of the reacting mass increases significantly with conversion. Thus, mixing and heat removal are the key process or reactor design factors. Also, the polymerization kinetics and mechanism are quite complex and often poorly understood despite many years of commercial production of vinyl polymers. This implies that depending on the particular chemical and physical characteristics of the polymer system, reactor types and process operating conditions must be properly designed and controlled.

Both batch and continuous reactors are used in industrial vinyl polymerization processes. Agitated kettles, tower reactors, and linear flow reactors are just a few examples of industrially used polymerization reactors. The choice of reactor type depends on the nature of polymerization systems, (homogeneous versus heterogeneous), the quality of product, and the amount of polymer to be produced. Sometimes, multiple reactors are used and operated at different reaction conditions. Whichever reactor system is used, it is always necessary to maximize the process productivity by reducing the reaction time (batch time or residence time) while obtaining desired polymer properties consistently.

For the industrial production of vinyl polymers, *mass (bulk)*, *solution*, *suspension*, and *emulsion* processes are commonly used. In the following, some important characteristics of these processes are briefly described.

Mass (bulk) Polymerization: If the polymer is soluble in its own monomer or solvent in all proportions [e.g., polystyrene, poly(methyl methacrylate), poly(vinyl acetate)], a single homogeneous phase is present in the reacting medium (homogeneous mass and solution processes). Some polymers such as poly(vinyl chloride), poly(acrylonitrile), and poly(vinylidene chloride) do not dissolve in their own monomers and they precipitate from the liquid almost immediately after the polymerization is started (heterogeneous mass process). Because no additives such as suspension stabilizer or emulsifier are necessary, the polymer prepared by mass process is in its purest form. However, the viscosity of the polymerizing mass increases rapidly and significantly with an increase in conversion in homogeneous bulk processes, making the mixing and the reactor temperature control difficult. Therefore, specially designed agitators are required to handle high-viscosity polymer fluid. In many industrial processes, mass polymerization is carried out in continuous reactors where monomer conversion is low and unreacted monomer is recovered and recycled. In heterogeneous mass processes [e.g., poly(vinyl chloride)], the final polymer product is recovered as a powder.

Solution Polymerization: Solution polymerization is usually carried out in a continuous-flow reactor system because of low-solution viscosity. Monomer is mixed with organic solvent and the polymer produced dissolved completely in the medium. The product from the solution process is used as a solution itself or as an intermediate for other applications. Because the

solution viscosity is low, heat transfer through the reactor jacket is efficient. The overall polymerization kinetics of solution polymerization are quite similar to those of bulk polymerization, except for the effect of solvent chain transfer. If chain transfer to solvent occurs significantly, polymer molecular weight decreases.

Suspension Polymerization: Most of the vinyl polymerizations are highly exothermic and the removal of reaction heat is an important reactor and process design consideration. In a batch suspension polymerization, which is often called *pearl* or *bead* polymerization, organic monomer is dispersed in water as discrete droplets (10 μm –5 mm) by mechanical agitation. Each droplet contains monomer(s), an organic-soluble initiator, a chain transfer agent, or other additives, and when heated to a desired reaction temperature, polymerization occurs to high conversion. The interfacial tension, the intensity of agitation, and the design of the stirrer and reactor system dictate the dispersion of monomer droplets. The aqueous phase serves as a suspension medium and also as a heat sink. The reaction heat released from the polymer particles is effectively removed by the water surrounding the polymer particles and, thus, isothermal reaction can be achieved. Therefore, the reactor temperature control in the suspension process is relatively easier than in the bulk process.

The liquid droplets dispersed in water undergo constant collision and some of the collisions result in coalescence. If the coalescence is not controlled or excessive, suspension stability is lost and undesirable particle agglomeration occurs. To prevent the coalescence or agglomeration of monomer droplets and polymer particles and to obtain uniform-sized particles, a suspension stabilizer (protective colloid or dispersant) is added to the aqueous phase. The most important issues in suspension polymerization are the control of polymer particle size distribution and the resulting polymer particle morphology. If the polymer is insoluble in its monomer [e.g., poly(vinyl chloride)], the heterogeneous polymerization takes place in the droplets and the development of particle morphology becomes quite complex. The kinetics of suspension polymerization are quite similar to those of mass polymerization. In suspension polymerization, mixing is critical to preventing the sedimentation of droplets due to the increase in density as polymerization proceeds. Any accumulation of stagnant mass at the bottom zone of the reactor may cause the increases in polymerization rate and heat generation, leading to the rapid monomer vaporization. Some critical issues on suspension polymerization have been reviewed recently [1,2].

Emulsion Polymerization: High polymerization rate and high polymer molecular weight are simultaneously obtainable in emulsion polymerization. Due to the heterogeneous nature of emulsion polymerization, chemical and physical phenomena in emulsion polymerization are far more

complex than in other polymerization processes. As in suspension polymerization, the monomer is dispersed in water by mechanical agitation as small droplets (0.05–2.0 mm) in emulsion polymerization. However, there are several fundamental differences between emulsion and suspension processes. In suspension process, polymerization occurs in each monomer droplet containing an organic-soluble initiator; in emulsion polymerization, negligible or no reaction takes place in the monomer droplets. It is required that monomer is only slightly soluble in water.

Particle nucleation and particle growth are important steps in emulsion polymerization because they affect the overall polymerization rate and polymer properties. Thus, initiator concentration and surfactant type/concentration have significant effects on the polymerization kinetics. In a batch emulsion process, particle nucleation and growth steps can be separated to some extent by employing a multistage reaction process. In a continuous process, both particle nucleation and growth steps occur simultaneously unless a seed reactor is provided to separate these two effects. In general, latex particle size distributions obtained by batch and continuous processes are quite different.

One of the key ingredients in emulsion polymerization is surfactant or emulsifier that has both hydrophilic and hydrophobic ends. The monomer droplets are stabilized by a monolayer of surfactant at the monomer–water interface. If the surfactant concentration exceeds a critical level (critical micelle concentration), the aggregates of surfactant molecules, called micelles, are formed. The size of micelles is about 100 Å which consists of about 5–100 surfactant molecules. The emulsifier molecules in the micelles are oriented so that the hydrophobic ends of the surfactant molecules are oriented toward the center of micelle while the hydrophilic ends extend out into the aqueous phase. Because the micelles are much smaller than the monomer droplets, the total surface area of the micelles is generally one to three orders of magnitude larger than that of the monomer droplets. As a result, the monomer droplets hardly absorb radicals from the aqueous phase and little reaction occurs in the dispersed monomer droplets. In emulsion polymerization, a water-soluble initiator such as potassium persulfate is used. Small amounts of monomer dissolved in the aqueous phase diffuse into the center of micelles. As the whole mixture in the reactor is heated, initiator decomposes in the aqueous phase to primary radicals. When a free radical generated in the aqueous phase is captured by the micelle-containing monomer, polymerization starts. As polymerization continues, more and more emulsifier is required to stabilize the growing monomer-swollen polymer particle until the micelles disappear. The monomer dissolved in water may polymerize to low-molecular-weight oligomers in the aqueous phase. These oligomers with chain length less than 5 may diffuse to growing latex

particles or they may be emulsified by surfactant molecules and form a new polymer particle. With an increase in monomer conversion, dispersed monomer droplets become smaller and the polymer latex particles become larger. The monomer concentration in monomer-swollen polymer latex particles remains constant when the separate monomer droplets are present in the aqueous phase. Eventually, the monomer droplets disappear and the polymerization rate decreases because no additional supply of monomer to polymer particles is available. Figure 1 illustrates the particle growth mechanism [3].

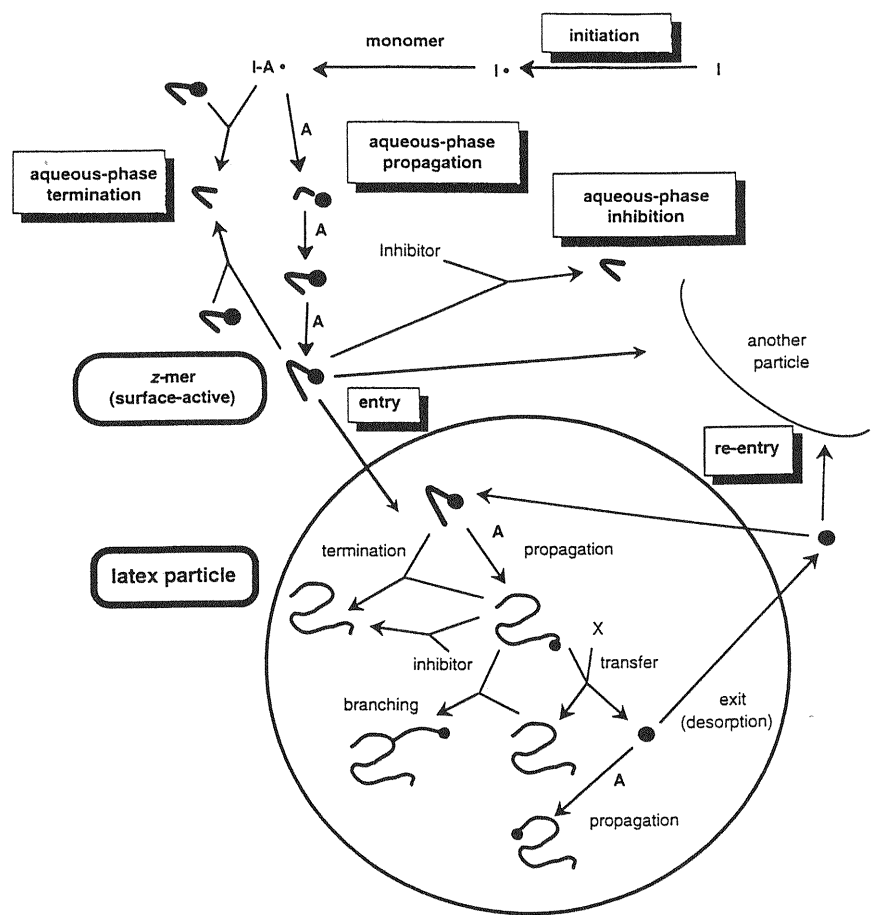


Figure 1 Particle growth in emulsion polymerization. (From Ref. 3.)

The emulsion polymerization kinetics have been the subject of extensive research since the 1940s, but there are still many aspects of emulsion polymerization that are not completely understood. The discussion of emulsion polymerization kinetics is beyond the scope of this chapter and there are many excellent references on emulsion polymerization kinetics [4,5].

In this chapter, various industrially important free-radical polymerization processes are reviewed. Table 1 presents the types of commercial polymerization processes for the polymers discussed in this chapter.

The manufacturing of the polymers to be discussed in this chapter are commercially well established. It is not the objective of this chapter to provide an extensive review of polymerization kinetics and mechanisms which are already well addressed or reviewed elsewhere. Instead, the discussion will be focused on the technical aspects of polymerization processes reported in open literature.

Although the polymerization processes for many vinyl polymers are well established, the polymer industry is continuously pursuing improved process technology. For example, batch reaction time or residence time (in a continuous reactor process) needs to be minimized while desired polymer properties are obtained. Consistency in the polymer product quality is another important process control objective in operating polymerization reactors. It is also desired that a product-grade slate should be diversified. However, achieving such goals is not always straightforward or easy. In many polymerization processes, polymer properties or quality control parameters are difficult to monitor on-line and making appropriate process adjustments

Table 1 Types of Commercial Polymerization Processes

Polymer	Homogeneous processes		Heterogeneous processes		
	Mass (Bulk)	Solution	Suspension	Emulsion	Mass (Precipitation)
Polyethylene	■				
Polystyrene	■	■	■	■	
Poly(methyl methacrylate)	■	■	■	■	
Polyacrylonitrile					■
Poly(vinyl chloride)			■	■	■
Poly(vinyl acetate)	■	■	■	■	
Poly(tetrafluoroethylene)			■	■	
Poly(vinyl/vinylidene chloride)		■	■	■	■

is not a trivial matter when some deviations in the product properties from their target values are detected. High exothermicity and process nonlinearity also cause the design and operation of polymerization reactors difficulty. The kinetics of polymerization, particularly those of heterogeneous polymerization, are often not completely understood. Recent academic and industrial research activities indicate that some of these problems can be solved by using process models in conjunction with advanced computer control techniques.

II. HIGH-PRESSURE ETHYLENE POLYMERIZATION PROCESSES

Low-density polyethylene (LDPE, $0.915\text{--}0.935\text{ g cm}^{-3}$) is produced industrially by either high-pressure free-radical polymerization or transition-metal-catalyzed low-pressure processes (e.g., gas-phase and slurry-phase Ziegler–Natta processes). Although the latter is gaining increasing popularity in recent years with the development of high-activity catalysts, high-pressure free-radical processes are still industrially very important and widely used. High-pressure polyethylene processes are characterized by high reaction pressure (1000–3000 atm) and high reaction temperature (150–300°C). Both stirred autoclave reactors and tubular reactors are commonly used in the industry. In Chapter 11, commercial high-pressure ethylene polymerization reactor systems are discussed. In general, tubular reactors give a more stable operation, whereas autoclave reactors often tend to be quite unstable with more frequent ethylene decomposition reactions. It has been known that polyethylenes made by different processes exhibit quite different molecular architecture and, hence, final end-use properties.

Low-density polyethylene manufactured by high-pressure free-radical polymerization technology is characterized by the presence of long-chain and short-chain branches. Polymer density, molecular-weight distribution, and branching frequencies (short chain and long chain) are strongly influenced by reaction pressure. The short branches are primarily ethyl and *n*-butyl groups. Up to 15 to 30 such side groups/1000 carbon atoms in the chain occur in LDPE. The number of short branches has a major effect on the density of polymer. Long-chain branches are much less frequent than short branches. The long-chain branches have important effects on polymer processability, clarity of polyethylene film, drawdown of coating resins, and service strength [6]. For typical polyethylenes, M_n (number-average molecular weight) is in the range 5000–40,000 and M_w (weight-average molecular weight) is in the range 50,000–800,000. With increasing pressure, propagation rate increases more rapidly than the termination rates and backbiting

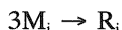
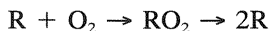
reactions leading to higher density, less branching, higher molecular weight, and fewer vinyl end groups.

Polyethylene made by high-pressure technology is often copolymerized with small amounts of comonomers (e.g., propylene, butene-1, hexene-1, octene-1, vinyl acetate, acrylic acid). The ethylene-vinyl acetate copolymers are used in film, wire or cable coating, and molding applications. Copolymers of ethylene and acrylic acid are treated with compounds of sodium, potassium, zinc, and so forth to form salts attached to the copolymer chain. Such copolymers are often called ionomers.

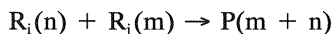
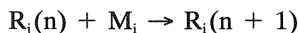
Some technological problems involved in building large LDPE production units are process operation, size of compressors, reactor structure, high-pressure valves, and safety problems [7]. Due to high exothermicity of the polymerization reaction, the removal of reaction heat is a critical design problem. Factors that affect the heat removal include: reactor surface/volume ratio, reaction mixture and feed ethylene temperature difference, thickness of the polyethylene layer at the inner wall of the reactor, reaction mixture flow rate, and reactor material heat conductance. It should be noted that the thickness of the laminar layer at the reactor wall is affected by the reaction mixture flow rate.

When ethylene is polymerized by free-radical mechanism, high pressure and high temperature are required. Organic initiators and oxygen are used as free-radical generators. The general kinetic scheme for free radical ethylene copolymerization is represented as follows:

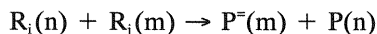
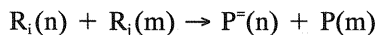
Initiation



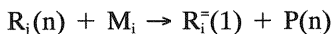
Propagation



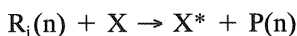
Chain termination



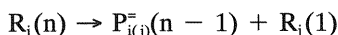
Chain transfer to monomer



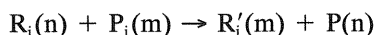
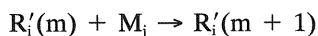
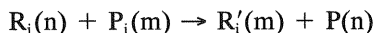
Chain transfer to chain transfer agent



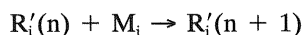
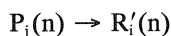
β -Scission of terminal radicals



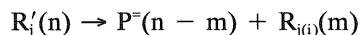
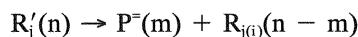
Chain transfer to polymer



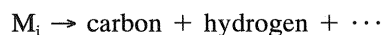
Backbiting (short-chain branching)



β -Scission of internal radical centers



Explosive decomposition



where I is the initiator, R is the primary radical, M is the monomer (ethylene), $R_n(n)$ is the growing polymer radical with chain length n ending with monomer j, $P(n)$ is the dead polymer with chain length n, and $P^-(n)$ is the dead polymer with chain length n and a terminal double bond.

As shown in the above, chain transfer to polymer, backbiting and β -scission reactions lead to long-chain and short-chain branches in the polymer. The intramolecular chain transfer reaction ("backbiting") occurs when the end of the polymer chain coils backward to abstract a hydrogen radical from the fifth carbon atom back in the polymer chain, and chain growth starts there. The intermolecular chain transfer to polymer leads to long-chain branching. The kinetic scheme shown above can be used to develop a comprehensive kinetic model to predict not only the polymerization rate or conversion but also the resulting polymer properties.

Sometimes, polymerization occurs in two phases (ethylene phase and polymer phase). The polyethylene produced in the polymer base is thought to be highly branched and of higher molecular weight. The degree of miscibility decreases as temperature is decreased.

In high-pressure polyethylene (PE) processes, a variety of free-radical generating initiators are used, depending on the polymerization temperature and the quality of the polyethylene to be produced. Because the initiator costs account for a significant fraction of total process operating costs, there is always a need to minimize the specific initiator consumption rate (grams of initiator injected per kilogram of PE produced) by employing optimal process operating conditions and initiator types. For some free-radical initiators used in high-pressure polyethylene processes (e.g., *tert*-butyl peroctoate, *tert*-butyl 3,5,5-trimethylperhexanoate, di-*tert*-butyl peroxide), it has been reported that the specific initiator consumption rate is a nonlinear function of reaction temperature. For example, as shown in Fig. 2, at low reaction temperatures, the specific initiator consumption rate decreases with increasing reaction temperature; however, as the reaction temperature is further increased, the specific initiator consumption rate increases. It is generally believed that such a nonlinear dependence of the specific initiator consump-

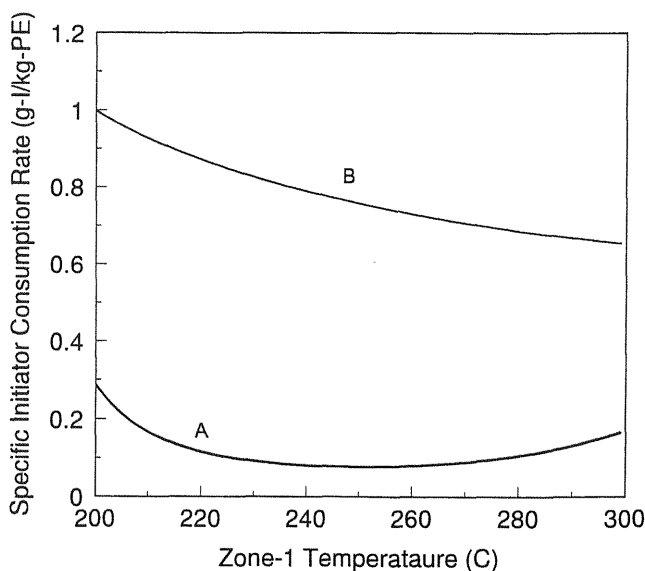


Figure 2 Specific initiator consumption rate for two common free-radical initiators. (From Ref. 8.)

tion rate on reaction temperature in a stirred autoclave reactor is due to imperfect mixing of the reacting fluid in the reactor.

A. Continuous Autoclave Reactors

In high-pressure autoclave processes, either single-stage or multistage reactor systems are used. Multistage reactors are advantageous in that the polymerization conditions in each compartment or reaction zone can be varied to broaden the product-grade slate. When a multistage or multicompartimented stirred autoclave reactor system is used, the reactor is typically a vertical cylindrical vessel with a large L/D ratio. A single initiator or a mixture of initiators is used. In a typical high-pressure process, fresh ethylene, after primary compression, is combined with recycled ethylene and with a comonomer. The mixture is then pressurized to the desired reactor pressure in the second compression stage. The reacting fluid (ethylene and polyethylene mixture) is intensely mixed by a agitator which consists of a vertical shaft to which impeller blades are attached to ensure efficient mixing of monomer, polymers, and initiators.

In general, the overall residence time is very short (1–3 min) and the reactor operates adiabatically. About 18–20% of monomer conversion is obtained. The heat of polymerization (21.2 kcal mol⁻¹) is removed by injecting cold monomer feed and by the bulk flow of ethylene and polyethylene mixture in the reactor. The reactor temperature is controlled by regulating the flow rate of initiator injected into the reactor. When a multistage reactor system is used, keeping the temperature in each zone at its desired level is important. This is because the resulting polymer properties (e.g., molecular weight, molecular-weight distribution, and short-chain and long-chain branching frequencies) are strongly dependent on reaction temperature as well as pressure and initiator type. Cold monomer feeds may be added to a few selected reaction compartments to remove additional reaction heat.

For a single continuous autoclave reactor of volume V to which ethylene and initiator are supplied, the following simple modeling equations can be derived:

$$\frac{dM}{dt} = \frac{1}{\theta} (M_f - M) - k_p MP \quad (1)$$

$$\frac{dI}{dt} = \frac{q_i}{V} (I_f - I) - k_d I \quad (2)$$

$$\frac{dT}{dt} = \frac{1}{\theta} (T_f - T) + \frac{(-\Delta H_r)}{\rho C_p} k_p MP \quad (3)$$

where θ is the residence time, T is the reactor temperature, T_f is the feed ethylene temperature, M_f is the feed ethylene concentration, M is the monomer concentration in the reactor, I_f is the feed initiator concentration, I is the initiator concentration in the reactor, k_p is the propagation rate constant, k_d is the initiator decomposition rate constant, q_i is the initiator feed rate, ΔH_r is the heat of polymerization, ρ is the fluid density, C_p is the fluid heat capacity, and P is the concentration of live radicals. At steady state, we can show from the above equations that the monomer conversion (x) is directly dependent on the reactor and ethylene feed temperatures as follows:

$$x = \frac{\rho C_p}{(-\Delta H_r) M_f} (T - T_f) \quad (4)$$

Notice that the monomer conversion is determined by the temperature difference between the reactor content and the monomer feed. It is also easy to show that the corresponding initiator feed rate is given by

$$q_i = \left(\frac{x}{\theta k_p (1 - x)} \right)^2 \frac{V k_t}{2\theta} \left(\frac{f_i k_d I_f}{1 + \theta k_d} \right)^{-1} \quad (5)$$

where k_t is the termination rate constant and f_i is the initiator efficiency factor (fraction of radicals available for chain initiation). Similar equations can be derived for a multizone reactor system.

In high-pressure ethylene polymerization, the kinetic rate constants are also dependent on pressure. For example, the propagation rate constant is given by

$$k_p = 4.8 \times 10^5 \exp \left(\frac{-4450 + 0.31P}{T} \right) \quad (6)$$

where k_p is in $\text{m}^3 \text{mol}^{-1} \text{sec}^{-1}$, P is in bar, and T is in K. It should be pointed out that there is a great deal of inconsistency in the reported values of the kinetic rate constants for high-pressure ethylene polymerization.

In autoclave processes, a mixture of fast initiator (low-temperature initiator) and slow initiator (high-temperature initiator) is used. Some examples of the commercial initiators used in high-pressure polyethylene processes are shown in Table 2.

When the reactor consists of more than one compartment, the behavior of downstream compartments are strongly dependent on those of upstream compartments. For the two-compartment continuous autoclave reactor, Fig. 3 illustrates the temperature of the second compartment as a function of the

Table 2 Examples of Commercial Initiators Used in High-Pressure PE Processes

Peroxide	Mol. wt. (g mol ⁻¹)	Active oxygen (wt%)	1-Hr half-life temperature (°C)
Fast initiators			
<i>t</i> -Butyl perneodecanoate	244.4	6.55	64
<i>t</i> -Amyl perneodecanoate	258.4	6.19	62
Di-(2-ethyl-hexyl)peroxy di-carbonate	346.5	4.62	47
Slow initiators			
Di- <i>tert</i> -butyl peroxide	146.2	10.7	147
Di- <i>tert</i> -amyl peroxide	174.2	8.7	142
<i>t</i> -Butyl hydroperoxide	90.1	14.1	200
3,4-Dimethyl-3,4-diphenyl hexane	266.2	—	210

first compartment for several volume ratios of the two compartments [8]. Here, the volume of zone 1 (first compartment) is fixed and only the zone 2 (second compartment) volume is varied. Notice that as the volume ratio is increased, the zone 2 temperature increases for a fixed zone 1 temperature, particularly in the zone 1 temperature range 200–250°C. For large zone 2 volumes, the fluid residence time increases, and as a result, more initiators decompose to radicals, which, in turn, accelerates the chain propagation reaction. Figure 3 also illustrates that the temperature difference between zone 1 and zone 2 is quite large for low zone 1 temperatures.

Although the high-pressure polyethylene process has been used in the polymer industry for years, there are still many aspects of the polymerization that are not completely understood. With a growing importance for tightly controlling the polymer properties or developing new polymer grades by changing the process operating conditions, the need for a thorough understanding of the process is becoming more important than ever.

One of the well-known phenomena in high-pressure polyethylene processes is a rapid ethylene decomposition reaction or thermal runaway, known as “decomp.” At 300°C, ethylene and even polyethylene decompose to carbon, methane, hydrogen, and other hydrocarbon by-products. When the decomposition reaction takes place, the reactor pressure builds up quickly and the reactor must be vented, shut down, and flushed for a long period of time before a new startup is initiated. The resulting economic loss will be quite

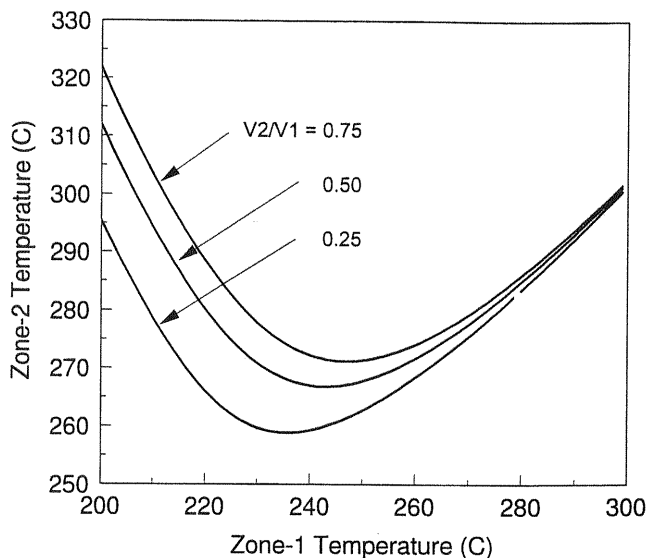
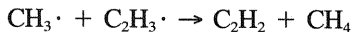
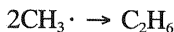
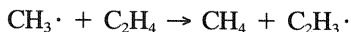
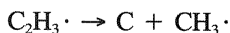
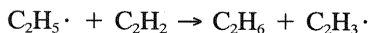


Figure 3 Effect of zone 2–zone 1 volume ratio on zone 2 temperature. (From Ref. 8.)

significant. The following reactions are believed to occur when ethylene is thermally decomposed [9]:



The thermal runaway can be caused by the formation of local hot spots. The causes for local hot spots are, for example, feed impurity, excess initiator in feed, poor feed distribution, inadequate mixing, mechanical friction, poor reactor temperature control system, feed temperature disturbance, and so forth [9]. Imperfect mixing in the polyethylene reactor has been considered as a primary cause for the runaway reaction phenomena. Short reactor residence time and comparable macromixing times may lead to imperfect

micromixing. Then, there can be different polymerization rates, and different concentration and temperature gradients in the mixing zones [10]. Recently, three-dimensional computational fluid dynamics (CFD) approach has been used by Read and co-workers [10] to analyze the micromixing phenomena in a single high-pressure LDPE reactor. According to their computer simulation study, characteristics of the autoclave reactor system include a steep concentration of the initiator profile close to the inlet, a temperature that increases going down the reactor, a maximum in the radical concentration, a conversion that increases down the reactor, and great sensitivity to the amount and composition of initiator.

In a stirred autoclave process, the polymerization is usually carried out in a single-phase region to facilitate the heat removal and to avoid fouling and forming cross-linked polymers. The presence of a viscous polymer-rich phase can also be the cause for the thermal runaway reaction via the autoacceleration effect [11]. When phase separation occurs in the reactor, chain termination in highly viscous polymer-rich phase becomes severely diffusion controlled, resulting in a rapid increase in the propagation rate.

Buildup of polymer deposits on the reactor surfaces often occurs if dead spots are present in the reactor. In the polymer deposits, polymerization and long-chain-branching reactions continue to occur, contributing to gel formation of fish eyes that decrease the polymer quality.

In some instances, polymerization is carried out in a two-phase region to produce LDPE exhibiting superior film properties because of narrower molecular-weight distribution and less long-chain branches. In an autoclave reactor, phase separation can be achieved by lowering the pressure or by adding an inert antisolvent such as nitrogen to the reaction mixture [12].

It should also be noted that recently a new high-pressure autoclave process has been developed by Exxon Chemical Company to produce linear low-density polyethylene using metallocene catalyst technology. Because the metallocene catalyst is a single-site catalyst, the molecular-weight distribution of the resulting polyethylene is very low ($M_w/M_n \approx 2.0$). The polymerization is carried out in a staged autoclave reactor at 1000–2000 atm and 150–250°C with 30–120 sec of reactor residence time [13].

B. Tubular Reactors

The tubular high-pressure ethylene polymerization reactor system consists of a long (more than a mile) narrow jacketed spiral tube with multiple feed streams along its length, ethylene compressors, and flash separators. To provide a plug flow profile in the reactor, a high length/diameter ratio (250–12,000) is used. For approximately 120,000 tons hr^{-1} plant, the tube diameter of around 50 mm is used. The unreacted ethylene in the polymerizing mixture is separated and recycled to the reactor. The polymerization pressure is typically of about 2500–3000 atm and temperatures in the range 150–

330°C, which is close to its safety limit (345°C). Compressed pure ethylene is mixed with a free-radical initiator (oxygen) and the reactor residence time is as low as 20 sec. The first section of the tubular reactor is heated because the heat generated by polymerization is insufficient. Because the fluid velocity is very high, a pressure drop along the tube length is significant and it affects the propagation rate. As a result, polymer molecular-weight distribution is broader than by using a stirred autoclave reactor [14].

For certain polymer grades, the inner reactor tube is fouled due to polymer deposition. The polymer deposition occurs due to the cooling of the reaction mixture through wall heat transfer. The fouling is faced mainly by increasing the coolant inlet temperature in the corresponding reactor jacket to melt the polymer wall deposits [15]. The time scale of the fouling–defouling cycles is about 2–12 hr. A common method for minimizing the fouling is the practice of pressure-pulsing the reactor. About once a minute, the pressure at the end of the reactor is suddenly dropped for several seconds by partially opening a special valve. The pressure pulse then transmits itself through the long tubular reactor, causing sudden increases in the flow velocities which tear the polyethylene deposits from the tube walls [6].

Because untreated ethylene is recycled, impurities may accumulate in the system that may affect the overall production of the primary radicals and the molecular-weight developments of the polyethylene product. Chain transfer agents such as ketones, aldehydes, alcohols, hydrogen, or chlorinated components may be added to narrow molecular-weight distribution.

In a tubular polyethylene reactor, the high-pressure valves are an important part of the process technology. For example, the difference in pressure at the release valve at the end of the tubular reactor can amount to 3000 atm. The temperature difference across the valve can be up to 60°C. When the release valve is opened, the flow increases severalfold and the regulating power of the valve must be very high and can be 100 megapounds. The valve adjusting must take place in milliseconds and must be exact to 10^{-3} mm [7].

After polymerization, the reacting mass is transferred to a high-pressure separator (150–200 atm). The polymer-rich stream withdrawn from the bottom of the high-pressure separator undergoes a second separation step at near-atmospheric pressures in a low-pressure separator. The phase separation in the high-pressure separator and in the separators of the recycle line makes it possible to remove the polymer or wax from the mixture. To improve the separation efficiency, the pressure or the temperature in the separators must be decreased. Then, the recycle gas contains only traces of wax, and a lower amount of ethylene remains dissolved in the polymer melt from the high-pressure separator.

Figure 4 illustrates the phase-equilibrium curves for mixtures of ethylene and two LDPEs of different molecular weights [16]. The cloud curves give the pressure at the cloud point when the mixture starts to separate. The coexistence curves give the composition of the phases. The left branch of a coexistence curve shows the composition of the ethylene-rich light phase and the right branch gives the composition of the polymer-rich dense phase.

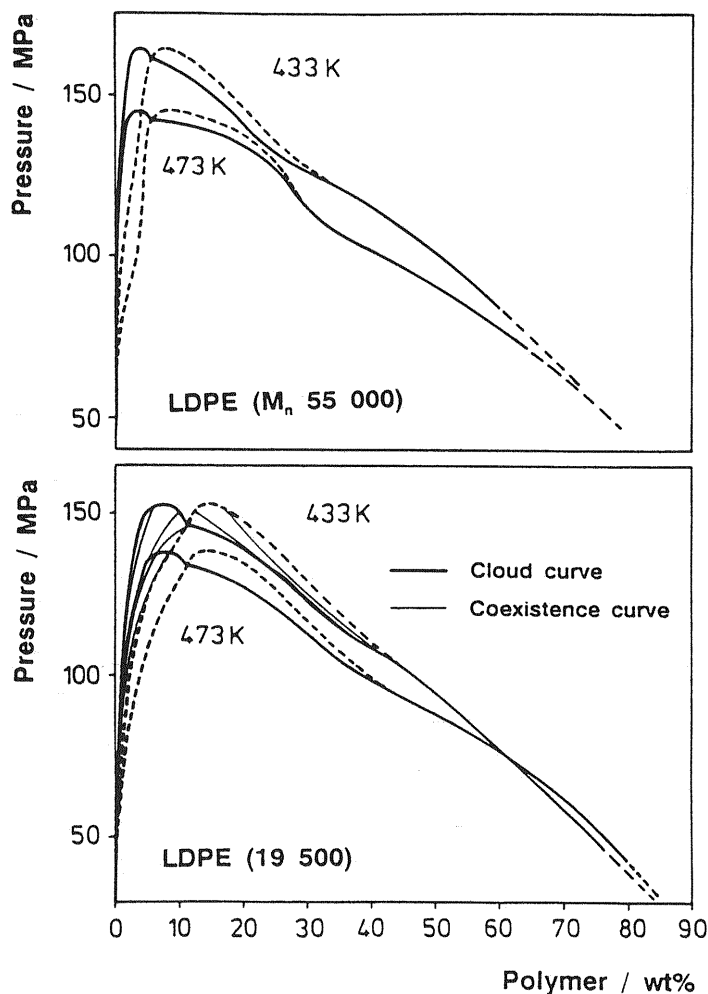


Figure 4 Phase equilibrium curves of ethylene and LDPE mixtures. (From Ref. 16.)

Outside the cloud curve, the mixture is homogeneous (single phase). Because polymers have a molecular-weight distribution, a phase separation in mixtures of polymers is always accompanied by a fractionation. As a result, the polymer in the polymer-rich phase has a higher polydispersity than the polymer in the ethylene-rich phase.

III. POLYSTYRENE

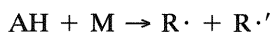
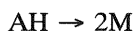
Polystyrene is one of the most important commodity polymers and perhaps the most well-known and most extensively studied polymers. Styrene can be polymerized by free-radical polymerization, ionic (cationic and anionic) polymerization, and coordination polymerization. Free-radical polymerization is most frequently used to produce atactic polystyrene. Ionic polymerization is used to prepare polystyrene of narrow molecular-weight distribution. Because styrene reacts readily with many other vinyl monomers and rubbers, a wide variety of styrene copolymers are commercially available. There are many styrene copolymers commercially available, but the following four styrene polymers are of particular importance:

- **Polystyrene homopolymer:** A clear, colorless, and brittle amorphous polymer (often called “crystal polystyrene” or “general-purpose polystyrene”)
- **Styrene–acrylonitrile copolymer (SAN):** A random copolymer having strong chemical resistance, heat resistance, and mechanical properties
- **High-impact polystyrene (HIPS):** An amorphous two-phase polymer with rubber particles in a polystyrene matrix to impart added impact strength
- **Acrylonitrile–butadiene–styrene copolymer (ABS):** A rubber-modified SAN copolymer. SAN forms the matrix phase and is grafted to a portion of the rubber.

The SAN and ABS copolymers contain approximately 25 wt% of acrylonitrile and polybutadiene rubber in amounts up to 20 wt%. Other styrene copolymers of industrial importance include styrene–maleic anhydride copolymer (SMA), styrene–divinylbenzene copolymer, acrylic–styrene–acrylonitrile terpolymer, and styrene–butadiene copolymer. Recently, metallocene catalysts have been developed to synthesize syndiotactic polystyrene (sPS). The polymerization process and process conditions have major effects on polymer properties and process economy. For styrene homopolymerization and copolymerization, various types of polymerization reactors are used commercially.

A. Styrene Homopolymerization

Polystyrene has a glass transition temperature of 100°C and is stable to thermal decomposition to 250°C. Styrene homopolymers are manufactured by suspension, mass (bulk), and solution polymerization processes. The polymerization can be initiated thermally at high temperatures or by a free-radical initiator. Typical molecular weights for polystyrene range from 200,000 to 300,000. When heated above 100°C, styrene generates free radicals and polymerizes to amorphous polystyrene. Thermal polymerization is advantageous in that because no additives are needed, the resulting polymers are pure. Thermal polymerization of styrene has been studied by many workers, and several reaction mechanisms have been proposed. Among them, the mechanism proposed by Mayo [17] is the most widely accepted. This mechanism involves the formation of the Diels–Alder adduct, followed by a molecular-assisted homolysis between the adduct and another styrene molecule:



where M is the monomer and AH is 1-phenyl-1,2,3,9-tetrahydronaphthalene (Diels–Alder adduct). The overall initiation rate is expressed as

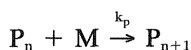
$$R_i = 2k_i M^3$$

The kinetic scheme for free-radical styrene homopolymerization initiated by a chemical initiator is represented as follows:

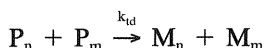
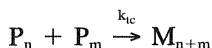
Initiation



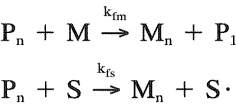
Propagation



Termination



Chain transfer



where I is the initiator, R is the primary radical, M is the monomer, P_n is the polymer radical with n monomer units, M_n is the dead polymer with n monomer units, S is the solvent.

In styrene polymerization, termination is mostly by combination (coupling). Quite often, a mixture of initiators or multifunctional initiators are used to achieve a high polymerization rate and a high polymer molecular weight [18–20]. Typical operating conditions for styrene homopolymerization processes are presented in Table 3 [21].

1. Suspension Polymerization

Suspension polymerization of styrene is mostly carried out in a batch reactor. A styrene monomer containing initiator(s) and chain transfer agents is dispersed in water as fine droplets by mechanical agitation. A blowing agent (e.g., *n*-pentane) can be added to the monomer if expandable polystyrene beads are desired. Each monomer droplet acts like a microbulk polymerization reactor. As polymerization proceeds, the monomer droplets become hard polymer particles or beads. To prevent the agglomeration of suspended particles, a water-soluble suspending agent is added. Because the heat generated in the suspended polymerizing particles can be dissipated effectively through water, temperature control is easier than mass (bulk) polystyrene process. The polymer particle size and its distribution are dictated by agitation, type of suspending agent, and its concentration.

A typical monomer/water ratio in suspension processes ranges from 1/4 to 1/1 and the particle size ranges from 0.1 to 1.0 mm. After polymerization, the polymer beads are washed with acid to remove initiator residue

Table 3 Typical Operating Conditions for Styrene Homopolymerization

Process	Temperature (°C)	Pressure	Reaction time (hr)
Suspension	110–170	Reduced	5–9
Mass (bulk)	80–200	Slightly reduced to 10–20 mmHg	12–18 (batch) 2–8 (continuous)
Solution	90–130	Atmospheric to 10–20 mmHg	6–8

and suspension stabilizers and pelletized using an extruder where any remaining monomer is further removed.

2. Mass (Bulk) Polymerization

Polystyrene manufactured by a mass process has high clarity and good electrical insulation properties. The main difficulties in polymerizing styrene by a mass process include heat removal and handling of a highly viscous polymerizing mass. If an initiator is used, the polymerization temperature is below 100°C, but a higher temperature is employed when the polymerization is thermally initiated. When a stirred tank reactor is used, monomer conversion per pass is limited to 30–50%. The polymerizing mass is transferred to an extruder/devolatilizer where unreacted monomer is recovered and recycled to the reactor. The stirred reactor is equipped with a reflux condenser operating under reduced pressure.

Both circulated and noncirculated tower reactors are used for bulk styrene polymerization. In a noncirculated tower reactor with no agitation device, styrene is polymerized in bulk to about 33–35% conversion. The reactor temperature profile is controlled from 100°C to 200°C by jackets and internal cooling coils. From the inlet to the reactor outlet, the temperature is progressively increased to reduce the viscosity of the polymerizing mass and to keep the polymerization rate high. In a noncirculated tower reactor system, more than one tower reactors are often used and the flowing reacting mass is slowly agitated. The product is discharged from the bottom of the tower by an extruder, cooled, and pelletized. A small amount of ethyl benzene (5–25%) may be added to a styrene feed stream to reduce the viscosity of a polymer solution and to ease heat transfer.

3. Solution Polymerization

In solution polymerization of styrene, the viscosity of the polymerizing solution is much lower than in the mass process; thus, temperature control is easier. Ethyl benzene is the most commonly used solvent and its concentration in the feed stream is about 5–25%. After polymerization, unreacted styrene and solvent are removed from the polymer and recycled. Three reactor types are used for solution polymerization of styrene as shown in Fig. 5 [22].

Continuous plug flow reactors such as recirculated stratified agitated tower reactors are multistaged, having a temperature profile of 100–170°C. Recirculated coil and ebullient reactors are single staged and operated isothermally.

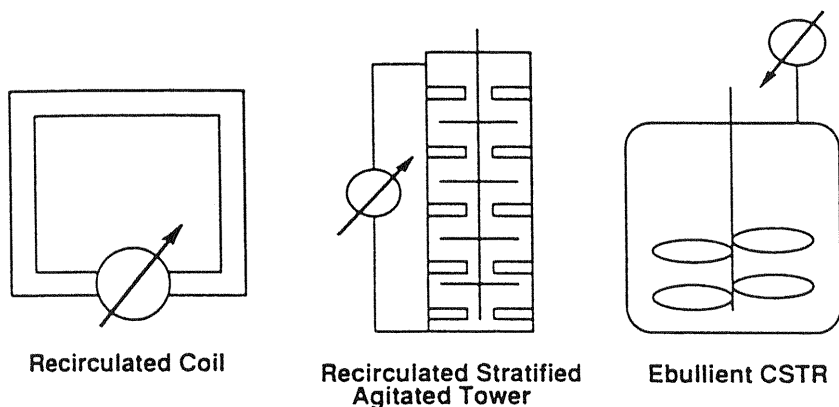
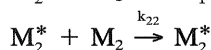
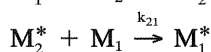
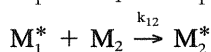
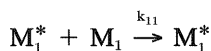


Figure 5 Continuous solution polymerization reactors. (From Ref. 22.)

B. Styrene Copolymerization

Styrene homopolymer is a brittle polymer. Styrene copolymers are industrially of significant importance because a wide variety of polymer properties can be obtained by copolymerizing styrene with rubbers (diens) and other vinyl monomers. When two vinyl monomers are copolymerized, the copolymer composition is determined by the following four propagation reactions:



where M_1 and M_2 are the comonomers, M_1^* and M_2^* are the polymer chain ending in a radical derived from an M_1 and M_2 monomer, respectively. The copolymer composition is determined by the reactivity ratios defined as

$$r_1 \equiv \frac{k_{11}}{k_{12}}$$

$$r_2 \equiv \frac{k_{22}}{k_{21}}$$

The mole fraction (F_1) of monomer M_1 in the polymer phase can then be expressed as follows:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{7}$$

where f_1 and f_2 are the mole fractions of monomer 1 and monomer 2 in the bulk phase, respectively. The reactivity ratios for various copolymerization systems are listed in the *Polymer Handbook* [23]. Quite often, different values of reactivity ratios are reported by different workers for the same copolymerization system. Equation (7) is valid for other binary copolymerization processes.

Figure 6 illustrates the copolymer composition curves for several styrene–comonomer systems. This figure shows that a high degree of composition drift and composition nonhomogeneity may occur in a styrene–acrylonitrile (SAN) copolymerization system for certain copolymer compositions.

When styrene is copolymerized with rubber to impact polymers (HIPS and ABS), rubber particles are imbedded into a polystyrene matrix. These soft rubber particles grafted onto a rigid polystyrene body are not compact

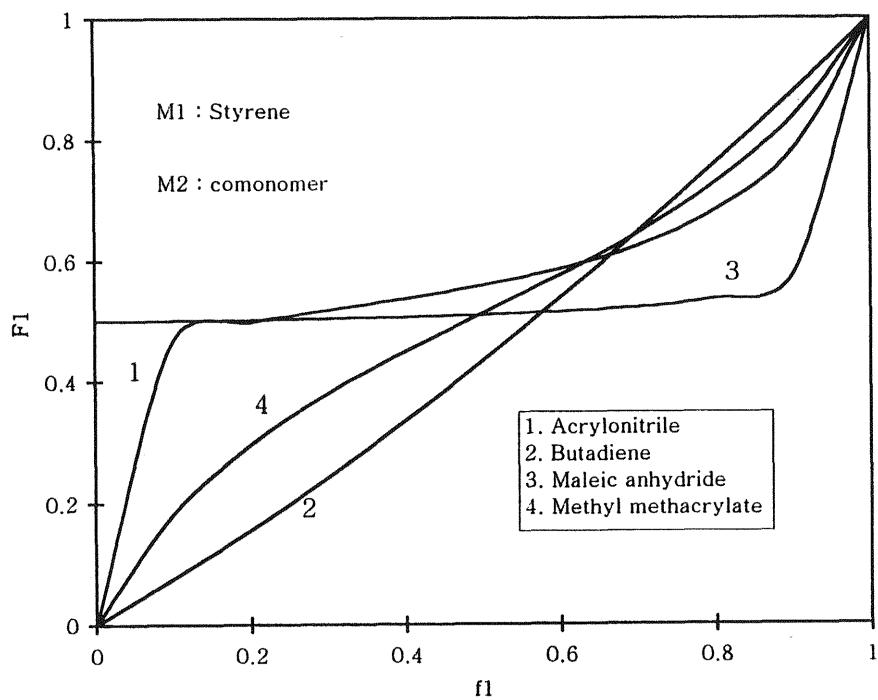
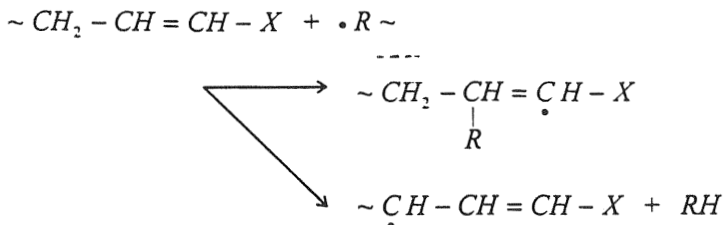


Figure 6 Copolymer composition curves.

but contain occluded matrix material. The grafting reaction can be schematically represented as



In graft copolymerization using an initiator, grafting occurs preferentially via the primary radicals, whereas in thermal graft copolymerization grafting is initiated by polymer radicals [24,25].

C. Styrene–Acrylonitrile Copolymer

The styrene-acrylonitrile (SAN) is one of the largest volume copolymers of styrene. SAN copolymers are amorphous, transparent, and glossy random copolymers produced by batch suspension, continuous mass (or solution), and emulsion polymerization processes. The molecular weight and the acrylonitrile content of the copolymer are the key factors in determining polymer properties. SAN has improved tensile yield, heat distortion, and solvent resistance than polystyrene because of the incorporation of acrylonitrile. For example, SAN is resistant to aliphatic hydrocarbons, alkalines, battery acids, vegetable oils, foods, and detergents. SAN is attacked by some aromatic hydrocarbons, ketones, esters, and chlorinated hydrocarbons [26]. Emulsion processes are used to produce SAN diluent for ABS resins. SAN produced by mass and suspension processes are primarily used for molding applications. A variety of copolymer properties or grades are available, depending on the molecular weight and the copolymer composition (styrene/acrylonitrile ratio).

The major problems in SAN processes are related to reactor temperature control, mixing, and copolymer composition control. The viscosities of concentrated SAN solutions are higher than polystyrene of the same molecular weight; thus, heat removal becomes more difficult. In a continuous reactor process, the mixing of low-viscosity feed streams and high-viscosity reacting fluid can be difficult. The polymerization rate is higher than that of styrene homopolymerization. If mixing is not homogeneous, SAN degrades, resulting in coloring and contamination. To avoid composition drift in a batch copolymerization process, SAN copolymers are often manufactured at the azeotropic point (see Fig. 6), where monomer and polymer have the

same composition. However, if the desired copolymer composition is not the azeotropic composition, the copolymer composition varies with conversion (or composition in the bulk phase). Composition drift in SAN copolymers is undesirable because SAN copolymers of different compositions are incompatible and cause phase separation. Therefore, it is crucial to monitor the bulk-phase composition and to make some corrective actions to prevent the copolymer composition drift. For example, more reactive monomer or comonomer can be added to the reactor during polymerization to keep the monomer/comonomer ratio constant. The polymerization reactors that can be used for continuous mass processes are loop reactors and continuous stirred tank reactors (CSTR) with an anchor agitator.

1. Emulsion Process

Both batch (or semicontinuous) and continuous emulsion processes are used to manufacture SAN latex. In a batch process, a styrene, acrylonitrile, and aqueous solution of a water-soluble initiator (e.g., potassium persulfate), emulsifier, and chain transfer agent (molecular-weight regulator; e.g., dodecyl mercaptan) are charged into a stirred tank reactor. The weight ratio of styrene/acrylonitrile is generally kept between 70/30 and 85/15. If the desired copolymer composition corresponds to the azeotropic composition, copolymer composition drift will be minimal. Otherwise, a monomer mixture having a different styrene/acrylonitrile ratio from the initial charge must be added continuously during polymerization to keep the ratio constant because any wall deviation in the bulk monomer phase composition can easily result in a significant composition heterogeneity. For example, two SAN copolymers differing more than 4% acrylonitrile content are incompatible, resulting in poor physical and mechanical properties [27]. To calculate the monomer feeding policy, a dynamic optimization technique can be used with a detailed process model [28]. In such a process, the reactor temperature can also be varied to minimize the batch reaction time while maintaining the copolymer composition and molecular weight and/or molecular-weight distribution at their target values.

In a continuous emulsion process, two or more stirred tank reactors in series are used. Separate feed streams are continuously added into each reactor. The reactors are operated at about 68°C. The latex is transferred to a holding tank (residence time of about 4 hr) before being steam-stripped to remove unreacted monomers. In a continuous process, the residence time distribution is generally broad. A large holding tank placed downstream of the reactors provides extra time to the reaction mixture and reduces the molecular-weight distribution.

2. Suspension Process

Suspension polymerization is carried out using a single reactor or two parallel reactors. A mixture of monomers, monomer-soluble initiator (peroxides and azo compounds), and any additives (e.g., chain transfer agents) is dispersed in water by mechanical agitation in the presence of a suspension stabilizer. The suspension polymerization temperatures ranges from 70°C to 125°C. The reactor temperature is increased gradually during the batch. SAN copolymer particles of 10–3000 μm are obtained. To keep the copolymer composition constant, a mixture of monomers is added into the reactor as in emulsion processes.

3. Mass Process

The mass process has some advantages over emulsion and suspension processes in that it is free of emulsifiers and suspending agents and thus produces SAN copolymers having higher clarity and good color retention. As no solvent is used, the viscosity of the reacting mass increases with conversion, and the removal of polymerization heat becomes a problem when the conversion of monomers exceed 60–70%. The mass polymerization is carried out in a jacketed reactor equipped with a reflux condenser at a temperature ranging from 110°C to 210°C. In a continuous process, 50–65% conversion obtained in a single reactor is further increased to 65–90% in the second reactor, which is typically a horizontal linear flow reactor. To handle the highly viscous reaction mass, the reaction temperature in the linear flow reactor is increased along the direction of flow. Mass polymerization can be initiated either thermally or chemically by organic initiators. The polymer product is fed to film evaporator, where unreacted monomers are recovered.

D. High-Impact Polystyrene

Styrene homopolymer is a rigid but brittle polymer with poor impact strength. Rubber is grafted to polystyrene to improve the impact strength of polystyrene. Fine rubber particles (0.5–10 μm) are dispersed in the polymer matrix. The incorporated rubber particles are cross-linked and contain grafted polystyrene. The inner structure of the polymer is determined by the polymerization process. Because the refractive indices of the rubber and the polystyrene phases are different, HIPS polymer is a translucent-to-opaque white polymer which exhibits high-impact strength and is resistant to wear. *Cis*-polybutadiene is the most common rubber used in the manufacture of HIPS. The properties of HIPS depend on the amount and type of rubber as well as many other reaction variables. Rubber particles that are too small or

too large may cause a loss of impact strength. A glossy HIPS polymer needs to balance the small particle size against impact strength. High rubber content, large particle size, high matrix molecular weight, and the choice of plasticizer improves the HIPS polymer's resistance to environmental stress crack agents [29].

Impact polystyrene is manufactured commercially by suspension, mass, and solution processes. In a mass process, polybutadiene rubber (2–5 μm) is dissolved in styrene. As styrene is polymerized, phase separation occurs and a rubber-rich phase and a polystyrene-rich phase are formed. The reaction mixture becomes opaque because of the difference in refractive indices between the two phases. Initially, polybutadiene in styrene is the continuous phase, and polystyrene in styrene is the discontinuous phase. When the phase volumes reach approximately equal volumes and sufficient shearing agitation exists, phase inversion occurs. Then, polystyrene in styrene becomes the continuous phase and polybutadiene in styrene becomes the discontinuous phase. At the phase-inversion point, a change in viscosity is observed [30]. The cohesion barrier attributable to the solution viscosity are overcome by the shearing agitation [31]. If shearing agitation is not adequate, phase inversion does not occur and a cross-linked continuous phase that produces gel is formed. Figure 7 shows a phase diagram of the

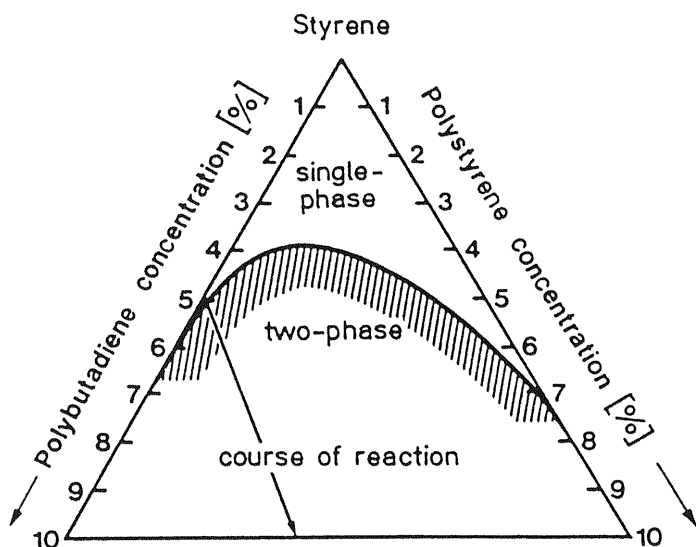


Figure 7 Phase diagram of styrene–polystyrene–polybutadiene system. (From Ref. 32.)

styrene–polystyrene–polybutadiene system [32]. The following equation has also been proposed to calculate the maximum degree of grafting (f) [33]:

$$f = \frac{V_R}{V_S} \ln \left(1 + \frac{V_R}{V_S} x \right) \quad (8)$$

where V_R and V_S are the phase volume of rubber and of polystyrene in styrene, respectively, and x is the conversion.

During polymerization, some of the free radicals react with the rubber, which is then grafted to the polystyrene chain. The grafting at the interface strongly affects particle size, morphology, and toughness of the polymer. The grafted rubber with its side chains accumulate at the interface between the two phases and function as an oil-in-oil emulsion stabilizer. Figure 8 illustrates various rubber particle structures in impact polystyrene [30].

The kinetics of graft copolymerization substantially correspond to those of styrene homopolymerization except at low rubber concentrations and at high conversions due to cross-linking reactions [34]. Figure 9 illustrates a schematic of a network of polybutadiene and polystyrene [35].

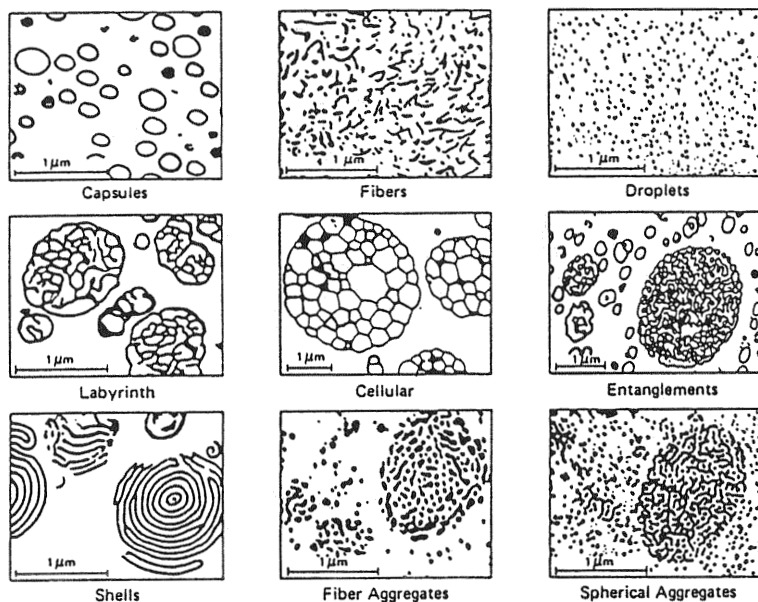


Figure 8 Various rubber particle structures in impact polystyrene. (From Ref. 30.)

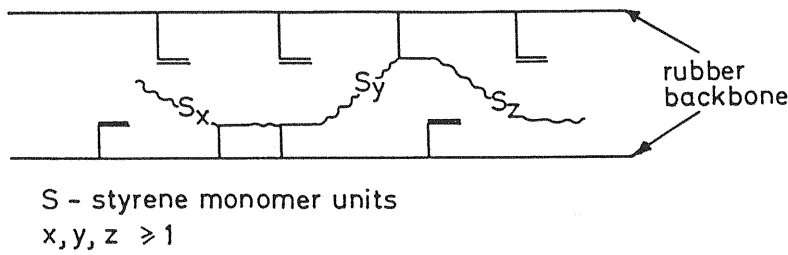


Figure 9 A network of polybutadiene and polystyrene. (From Ref. 35.)

At high conversions, the solvation of the rubber and the gel effect (Trommsdorf effect) cause an increase in the molecular weight of the grafted polystyrene. The viscosity change with styrene conversion in the manufacture of HIPS is shown in Fig. 10 with typical rubber particle morphology [34].

Like a styrene homopolymer, HIPS are manufactured commercially by continuous processes using agitated tower reactors, a stratifier, and back-mixed reactors [36–40]. HIPS polymers are often manufactured by a multistage process. Figure 11 illustrate a continuous mass process for the manufacture of impact polystyrene [40]. In the first stage (prepolymerizer), operating at 125–140°C, a solution of rubber and styrene is charged into the reactor with initiator, antioxidants, and other additives. Dissolving rubber in styrene is a slow process and must be done with enough shearing agitation

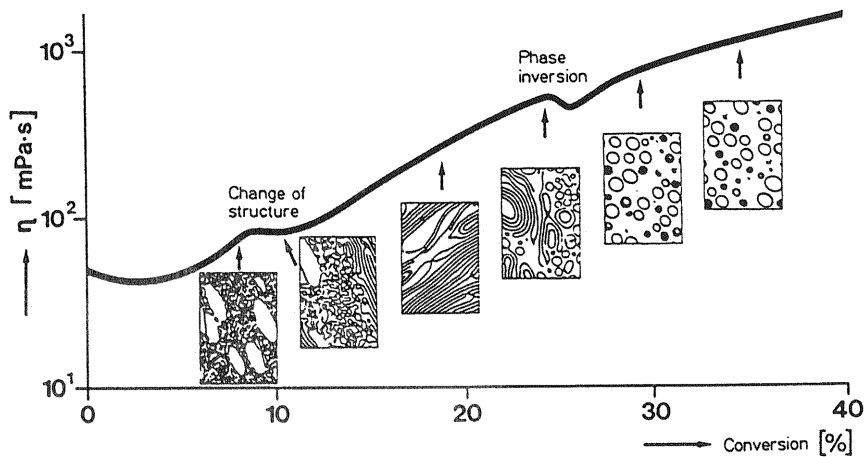


Figure 10 Viscosity–conversion curve for HIPS process. (From Ref. 34.)

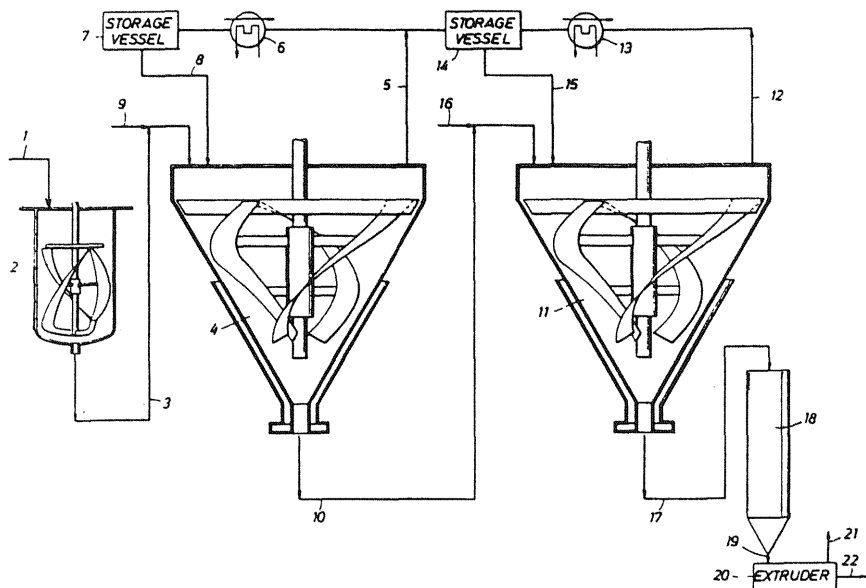


Figure 11 Continuous mass impact polystyrene process. (From Ref. 40.)

to effect phase inversion and to adequately size the rubber particles. The phase inversion occurs in the first stage. The polymerization is carried out to a conversion which is close to the point where increasing viscosity seriously limits mixing and temperature control. The agitation in the prepolymerization reactor must be sufficient to shear rubber particles. The speed of the agitator necessary to develop the shear is determined by the viscosity of the reaction medium which is a function of the temperature and the conversion level. The total monomer conversion in this stage is from about 25% to 35%. The product from the prepolymerization stage is then transferred to the second-stage reactor (intermediate zone), where the maximum monomer conversion reaches about 65–85% at 140–160°C. In the two second-stage reactors shown in Fig. 11 (marked by 4 and 11), styrene vapor is condensed and recycled. The third-stage reactor (final polymerizer) is a vertical or horizontal cylinder or tower reactor. It is an adiabatic plug flow reactor in which 85–90% conversion is reached. To ensure plug flow, only very slow stirring is allowed. In a vertical reactor, the polymerizing mass from the second stage is fed to the top of the reactor and flows downward. The temperature of the reacting mass increases gradually from 175°C to 215°C.

Figure 12 illustrates another example of a continuous bulk HIPS process where the polymerization is carried out in multiple stages [41]. Rubber

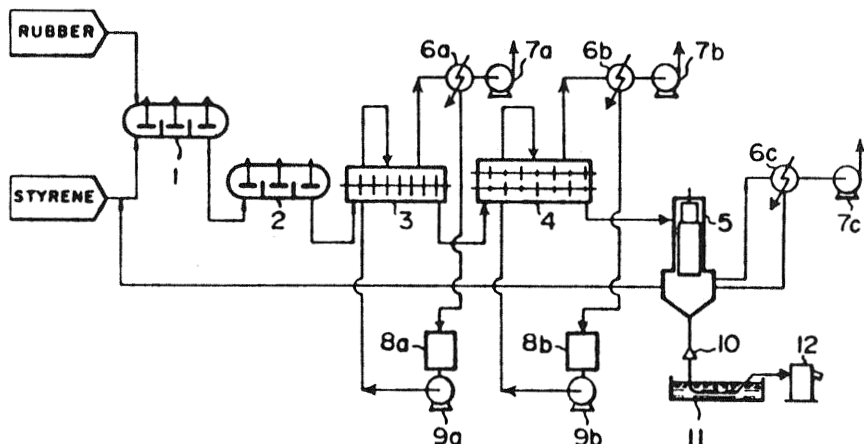


Figure 12 Continuous mass HIPS process. (From Ref. 41.)

is dissolved in styrene in the first stage operating under atmospheric pressure at temperatures raised stepwise from 20°C to 110°C. Then, the rubber solution is polymerized in the second stage (prepolymerization stage) at 100–130°C under atmospheric pressure to effect the phase inversion of rubber. The conversion in the prepolymerization stage is controlled in the range 25–40% and the polymerization heat is removed by use of an external cooling jacket. The prepolymer is further polymerized in the third stage at 100–200°C under reduced pressure, and the conversion is controlled in the range 45–60%. In this reactor, the reaction heat is removed by spraying the monomer onto the solution. The evaporated monomer is condensed and recycled. In the final-stage polymerization reactor, polymerization is carried out at 100–230°C at 1 atm to obtain 70–85% conversion.

The following correlation has been proposed for the calculation of the apparent viscosity of a HIPS prepolymer system [42]:

$$\frac{1}{\eta} = \frac{0.696(1 - \phi_{ps})}{\eta_R + 0.311(\phi_{ps}/\eta_{ps})} \quad (9)$$

where ϕ_{ps} is the polystyrene/styrene phase volume, η_R is the rubber phase viscosity, and η_{ps} is the polystyrene phase viscosity.

Impact polystyrene can be prepared by suspension polymerization. However, there is no shearing agitation within the individual polymer particles. Thus, a prepolymerization with shearing agitation needs to be carried out before suspension polymerization to obtain good polymer properties.

E. ABS Processes

ABS originally stands for a acrylonitrile–butadiene–styrene terpolymer. However, ABS is now used as a general term for a class of multicomponent polymers containing elastomeric rubber particles dispersed in a matrix of rigid copolymer. Because rubber particles and rigid copolymer matrix are incompatible, mechanical blending of rubbers with rigid vinyl copolymers is not effective. Instead, elastomeric rubber particles (polybutadiene rubber, styrene–butadiene rubber, acrylonitrile–butadiene rubber) are grafted by styrene and acrylonitrile copolymer. Typically, a grafting efficiency of 30–40% provides optimal polymer properties. Grafting occurs by direct attack of initiator radicals through hydrogen abstraction, and chain transfer onto the rubber polymer through double bonds. The degree of grafting is proportional to the surface area of the dispersed rubber particles. Because the surface/volume ratio increases with a decrease in particle size, a higher degree of grafting is achieved with smaller rubber particles. Process parameters that influence the degree of grafting are the concentrations of monomers, chain transfer agent, surfactant, polymerization temperature, and monomer/rubber ratio. The lower the monomer concentration and monomer/rubber ratio, the higher the grafting efficiency becomes. The degree of grafting is increased with an increase in reaction temperature, whereas it decreases with an increase in surfactant concentration. Increased rubber content and larger rubber particle size give rise to higher impact strength. ABS having a higher impact strength generally lowers tensile strength and modulus, and heat resistance. Other than impact strength, the following properties are important in manufacturing ABS: surface gloss, heat distortion temperature, flame retardancy, and weatherability.

The ABS graft polymers are commercially produced by emulsion polymerization and mass suspension polymerization processes although solution polymerization is used for some special type of polymer. A continuous emulsion–mass process has also been developed recently. In general, ABS manufactured by the emulsion process exhibits higher impact strength than the polymer by the mass suspension process.

1. Emulsion Polymerization

The emulsion polymerization process (batch or continuous) is widely used for producing ABS because various grades of ABS resins can be manufactured. In a continuous process, two to six reactors are used in series with rubber latex feed added either to the first reactor or the first two reactors. In a typical ABS emulsion process, the styrene/acrylonitrile copolymer (SAN) and polybutadiene (PBL) are separately prepared by emulsion pro-

cesses. More than one reactor can be used to produce PBLs of different rubber particle sizes (e.g., 0.1 μm and 0.4 μm). The two PBL lattices are separately graft polymerized and the resulting lattices are steam-stripped. Then, they are blended with SAN latex, coagulated, dewatered, and dried.

The monomer feeds containing monomers, a water-soluble initiator (e.g., potassium persulfate and redox systems), chain transfer agents (e.g., *tert*-dodecyl mercaptan), and an emulsifier [e.g., disproportionated potassium and sodium rosinsates, tridecycloxy(polyoxyethylene)phosphate] are separately added to each reactor. A rubber latex may also be imbibed with styrene or styrene/acrylonitrile mixture before the mixture is charged to the first reactor. In a batch process, monomers with initiator and chain transfer agents are often added continuously during the batch operation. The rubber lattices used in the emulsion polymerization process contain a high concentration of butadiene (60–90%) and have a solid content of 20–50% with an average latex particle size of 0.2–0.4 μm . To obtain a bimodal rubber particle size distribution in the resulting rubber latex, a mixture of two lattices, one having a large and the other a small particle size, may be used. In general, styrene/acrylonitrile weight ratio ranges from 25/75 to 40/60, but for the production of ABS with high styrene content, a styrene/acrylonitrile ratio ranging from 70/30 to 75/25 is employed and the ratio is kept constant during polymerization. Methyl acrylate and methyl methacrylate are also used to make a highly transparent graft polymer. To prepare the polymer with a high acrylonitrile content, water-insoluble azo compounds are used to minimize the polymerization of acrylonitrile in aqueous phase due to the high solubility of acrylonitrile in water.

2. Mass Suspension Polymerization

The mass suspension polymerization process requires a lower investment than the emulsion process. The mass suspension ABS polymers have better melt flow characteristics and light stability. In general, ABS manufactured by the mass suspension process exhibit low impact strength, poor surface gloss, and poor weatherability. To improve impact strength and gloss, they are often blended with emulsion ABS resin in a mixture of styrene and acrylonitrile. The resulting dispersion is then blended with a second dispersion prepared by an organic extraction of the ABS latex with a mixture of styrene and acrylonitrile. The blended dispersion is then devolatilized to remove monomers and extruded into polyblend resin pellets. High shearing forces may also be applied during the mass polymerization stage to reduce the rubber particle size and, thus, to improve surface gloss.

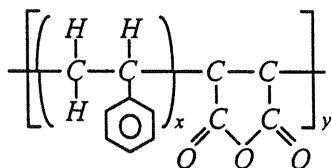
The mass suspension ABS polymerization process consists of two stages. In the first-stage mass polymerization, 5–15% rubber (polybutadiene or SBR containing about 75% butadiene) dissolved in styrene is graft polymerized with styrene and acrylonitrile at 98–115°C without an initiator or at 70–95°C with an organic-soluble initiator for 3–6 hr to about 20–35% conversion. The reaction mass is then transferred to a second-stage suspension polymerization reactor. In the suspension reactor, polymerization is carried out at higher temperatures (80–150°C) in the presence of organic initiator(s). Polyvinyl alcohol (PVA) is commonly used as suspension stabilizer. In batch processes, the polymerization temperature is gradually increased during the batch to achieve a high conversion of monomers.

3. Mass Polymerization

Mass polymerization can be thermally initiated or initiated by organic peroxides. The polymerization temperature, generally higher than that of emulsion polymerization, is increased in stages from 100°C to as high as 240°C. In a continuous mass process, grafted rubber dispersion and monomers are fed to a jacketed reactor equipped with a helical ribbon-type agitator and a reflux condenser. The prepolymer is then transferred to the second-stage polymerization reactor equipped with an agitator specially designed to form a plug flow. The reaction temperature is gradually increased as the polymer mass flows. The reaction product is continuously charged to a vented extruder and pelletized.

F. Styrene–Maleic Anhydride Copolymers

When styrene is copolymerized with maleic anhydride which does not homopolymerize, a completely alternating copolymer is obtained. Maleic anhydride, randomly incorporated into the polystyrene backbone, increases the glass transition temperature and heat distortion temperatures (>260°F). The copolymers are stable during injection molding to temperatures above 550°F [26].



G. Syndiotactic Polystyrene by Metallocenes

With recent developments of metallocenes for α -olefin polymerization, the synthesis of syndiotactic polystyrene (sPS) with metallocene catalysts has attracted strong research interest. Although isotactic polystyrene was synthesized in the 1950s by Natta et al. [43] with a $\text{TiCl}_4/\text{Al}(\text{C}_2\text{H}_5)_3$ catalyst [42], the polymer is highly crystalline with a melting temperature of 240°C and its crystallization temperature was too slow for any commercial applications. The synthesis of sPS was first reported by Ishihara and co-workers [44]. Syndiotactic polystyrene is a highly crystalline polymer with a melting temperature of about 270°C . Its glass transition temperature is similar to atactic polystyrene. However, unlike isotactic polystyrene, syndiotactic polystyrene exhibits a relatively fast crystallization rate, low specific gravity, low dielectric constant, high elastic modulus, and excellent resistance to chemicals. The sPS may find some applications in the automotive, electronic, and packaging industries. Since sPS is brittle when used alone, sPS needs to be reinforced with fiberglass, fillers, or elastomers to be used as structural material.

Syndiotactic polystyrene can be prepared using group IV metal (Ti, Zr) compounds and methylaluminoxane (MAO). It has been suggested that Ti^{3+} species are the active site for producing sPS. Aluminum alkyls are ineffective for preparing syndiotactic polystyrene. The syndiotactic configuration of polystyrene arises from phenyl–phenyl repulsive interactions between the last inserted monomer unit of the growing chain and the incoming monomer. However, it is generally known that zirconium compounds are less active and efficient than titanium compounds. A large number of catalytic compounds or compositions have been investigated by many researchers, and different catalysts exhibit different polymerization kinetic behaviors and polymer properties. Also, it is still an active research area. Therefore, it is not easy to generalize the syndiotactic styrene polymerization kinetics. An excellent review of recent literature on the synthesis of syndiotactic polystyrene has been published by Pó and Cardí [45].

Syndiotactic polystyrene is prepared in an organic diluent such as toluene. As the reaction progresses, gellike or solid precipitates are formed, and the reaction proceeds in a heterogeneous phase. Due to the formation of solid polymers insoluble in diluent liquid, it is thus important to control fouling formation in a polymerization reactor. The polymer recovered is treated with acidified alcohol to deactivate the catalyst. The product polymer contains some atactic polystyrene which is extracted out in boiling acetone or methylethylketone (MEK). It has been reported that the fraction of syndiotactic sites is far smaller than atactic sites (1.7% versus 20% of total titanium), and the syndiospecific propagation rate constant is far larger than the propagation rate constant for atactic sites [46,47]. Some authors suggest

that syndiospecific active sites change into aspecific sites at high reaction temperatures. The syndiotactic fraction is often measured by a MEK-insoluble fraction. Nuclear magnetic resonance is used to determine syndiotacticity, which represents the percentage of syndiotactic sequences (either diads, triads, tetrads, or pentads) relative to the total number of sequences along the polymer chain.

IV. POLY(METHYL METHACRYLATE) AND COPOLYMERS

Acrylic homopolymers $[(\text{—CH}_2\text{CH}(\text{COOR})\text{—})_n]$ and copolymers are synthesized from acrylates and methacrylates. Through copolymerization, the polymer properties are widely varied from soft, flexible elastomers to hard, stiff thermoplastics and thermosets. Acrylic polymers are produced in many different forms including sheet, rod, tube, pellets, beads, film, solutions, lattices, and reactive syrups.

The poly(methyl methacrylate) (PMMA) homopolymer is completely amorphous and has high strength and excellent dimensional stability due to the rigid polymer chains. PMMA has exceptional optical clarity, very good weatherability and impact resistance, and is resistant to many chemicals. PMMA is manufactured industrially by bulk, solution, suspension, and emulsion processes. The bulk polymerization is used to manufacture PMMA sheets, rods, tubes, and molding powders. The solution polymerization is used to prepare polymers for use as coatings, adhesives, impregnates, and laminates. Small polymer beads (0.1–5 mm) made by suspension polymerization are used as molding powders and ion-exchange resins. MMA is often copolymerized to reduce brittleness and improve processability. Emulsion polymerization is used to produce aqueous dispersion of polymers for paint, paper, textile, floor polish, and leather industries. Typical operating conditions for various MMA polymerization processes are presented in Table 4.

Table 4 Typical Operating Conditions for Some MMA Polymerization Processes

Process	Temperature (°C)	Reaction time (hr)	Conversion (%)
Mass	30–90	8–24	20–50
Solution	136–143	6–8	>95
Suspension	30–75	3–6	>95
Emulsion	25–90	>2.5	>95

A. Bulk Polymerization

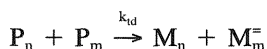
When pure MMA is polymerized, viscosity increases significantly and the Trommsdorf effect (diffusion-controlled termination, autoacceleration) becomes pronounced. Thus, conventional stirred reactors are inadequate for the bulk polymerization. The PMMA sheet is made by bulk (or cast) polymerization of MMA with an organic initiator (peroxide or azo compounds) in a mold consisting of two glass plates separated by a flexible gasket that is also the confining wall of the mold. The entire mold assembly is placed in an air oven and heated. In this process, clear liquid monomers or partially polymerized homogeneous syrups are polymerized directly into shapes such as sheets, rods, tubes, or blocks. Polymers manufactured by bulk process are normally better in clarity, homogeneity, and color than those produced by other processes such as suspension, solution, and emulsion. Due to the high reaction exotherm, the boiling monomer may leave bubbles in the sheet and some shrinkage occurs on polymerization. Thus, the polymerization is carried out below the boiling point of MMA (100.5°C).

In a continuous sheet-casting process, the casting syrup is confined between stainless-steel belts by using a flexible gasket and the belts run progressively through polymerization and annealing zones. The belt moves at about 1 m min^{-1} , which results in about 45 min of residence time in the curing zone (70°C) and about 10 min in the annealing zone (110°C) [48]. Pressure is maintained to prevent the boiling of MMA monomer.

B. Suspension Polymerization

Methyl methacrylate mixed with a small amount of initiator is dispersed in water by agitation as 0.1–5-mm droplets, stabilized by organic or inorganic protective colloids or surface stabilizer. The monomer/water ratio generally ranges from 50/50 to 25/75. Lower ratios are not practical for economical production. The reactor content is heated under a nitrogen atmosphere to the desired polymerization temperature. The heat of polymerization is effectively dissipated from the polymerizing droplet to the aqueous phase. Each droplet can be viewed as a microbatch bulk polymerization reactor, and the bulk MMA polymerization kinetics can be applied. As monomer conversion increases, the polymer particles become sticky and they tend to agglomerate.

The chain termination in methyl methacrylate polymerization is almost exclusively via a disproportionation mechanism:



where P_n is the growing polymer radical, M_n is the dead polymer, and $M_m^=$ is the dead polymer with a terminal double bond. It is important to achieve

a high monomer conversion because the removal of unreacted monomer from polymer is difficult.

In batch suspension polymerization, controlling the polymer particle (bead) size and its distribution is important. In the early stage of suspension polymerization, the monomer droplet size is determined as a result of the dynamic equilibrium between breakage by shear or turbulence forces and coalescence by interfacial tension or adhesion forces [49]. As the shearing action in an agitator reactor can be nonuniform, an equilibrium condition is only possible if all the particles move through a zone of maximum shear. The elastic deformation of colliding particles may produce a greater surface disturbance, leading to a fusion of droplets or particles. Several empirical correlations are available for the estimation of particle size in suspension polymerization [2]. The polymer particle size and distribution are strongly affected by geometric factors (e.g., reactor type, reactor height/diameter ratio, stirrer type and geometry, baffle, etc.), reactor operating parameters (e.g., reaction time, stirrer speed, monomer/water ratio, temperature, stabilizer type and concentration, additives, etc.), and physical properties of the aqueous phase (e.g., interfacial tension, density, viscosity, pH, etc.) [2]. For example, particle size distribution becomes narrower and shift toward smaller sizes with increases in stirring speed and suspending agent concentration. At lower temperatures, the particle size distribution is controlled by the viscosities of the dispersed phase and the aqueous phase at a fixed agitator speed; thus, lower temperatures favor larger particles. At higher temperatures, the polymerization rate is so high that the viscosity of the dispersed phase (droplets) is increased before the droplets reach their equilibrium size and the particle size increases with temperature. The average polymer particle size decreases as stabilizer concentration or agitation speed is increased [49].

In suspension polymerization operation, the detection of suspension failure is important. In general, the first indications of suspension failure are abnormal agitator drive power readings; however, this does not occur until polymer buildup on and/or near the agitator is sufficient to disturb the mixing behavior [50].

Suspension polymerization of MMA is industrially carried out using batch reactors. Although there is some literature on continuous suspension polymerization processes, no large-scale continuous suspension process is currently used in industry. Some problems of continuous suspension polymerization are achieving high monomer conversion, avoiding fouling of the reactor wall and pipes, and achieving polymers with the desired particle size distribution and molecular-weight distribution [51]. Technically, narrow residence time distribution is necessary to obtain high conversions, and good mixing of the two phases is important to obtain polymers with the proper

particle size distribution. To avoid fouling, dead space should be avoided [52].

C. Solution Polymerization

Solution polymerization of acrylic esters are usually carried out in large agitated reactors in an organic solvent. Both propagation and termination rates are affected by the nature of the solvent, but the rate of initiator decomposition is almost independent of the solvent. It has been reported in literature that solvents such as benzene, toluene, and xylene enhance the rate of MMA polymerization. A typical recipe for the copolymerization of MMA is presented in Table 5 [48]. The solution polymerization is conducted at 140°C by adding the monomer and initiator mixture uniformly over 3 hr. After the addition of reactants is complete, the reaction is continued for 2 more hours at the same temperature.

The autoacceleration effect (Trommsdorf effect) is less pronounced in solution polymerization than in bulk or suspension polymerization due to lower viscosity of the polymerizing solution. To prevent a thermal runaway reaction, the reactants are often added gradually to the reactor. The polymer molecular weight is controlled through the use of a chain transfer agent and by initiator concentration and type. Monomer concentration, solvent type, and reaction temperature also affect the molecular weight.

D. Emulsion Polymerization

Emulsion homopolymerization or copolymerization of MMA is usually carried out in a pressurized batch reactor with a water-soluble initiator and surfactant. The polymerization temperature may be varied from 85°C to 95°C to achieve high conversion. Bacterial attack, common in acrylic polymer

Table 5 Typical Recipe for the Copolymerization of MMA

Materials	Parts
Xylene (solvent)	28.4
Ethoxyethanol (solvent)	14.1
Methyl methacrylate (monomer)	23.3
2-Ethylhexyl methacrylate (comonomer)	15.5
Hydroxyethyl methacrylate (comonomer)	17.6
<i>tert</i> -Butyl perbenzoate (initiator)	1.1

latex, can be avoided by pH adjustment and the addition of bactericidal agents.

V. POLYACRYLONITRILE

Acrylonitrile is readily polymerized to polyacrylonitrile ($-[\text{CH}_2\text{CH}(\text{CN})]-$) by free-radical polymerization with organic initiators (peroxides and azo compounds). Rigidity, low permeability, high tack as adhesives, strong resistance to chemicals and solvents, heat resistance, and so forth are mostly due to the polar nature of polyacrylonitrile. Polyacrylonitrile is often copolymerized with halogen-containing monomers (e.g., vinyl chloride, vinylidene chloride) to impart flame retardancy. The nitrile group may also be reactive, leading to a colored naphthyridine group [53].

Like poly(vinyl chloride), polyacrylonitrile does not dissolve in its own monomer; hence, when bulk polymerized, the polymer precipitates from the monomer solution. The precipitated polymer particles, if not stabilized, tend to agglomerate to form a polymer paste or slurry. There are two polymerization reaction loci: a polymer-free monomer phase and a polymer phase containing dissolved monomer. The polymer phase may be saturated with monomer. The physical properties of the polymer and monomer phase have a significant effect on the polymerization rate. The polymer particles formed in bulk polymerization of acrylonitrile consist of polymeric phase made up of 94% polyacrylonitrile and 6% acrylonitrile [54]. Due to its extremely low solubility in acrylonitrile, the polyacrylonitrile polymer is believed to grow on the polymer particle surface from the very low conversion. If the coagulation of initial small precipitated particles occurs, the reaction site will be either the outer or inner surface of a coagulated particle.

The polymerization of acrylonitrile also exhibits strong autocatalytic behavior (Trommsdorf effect), making the heat removal difficult as conversion increases. The autocatalytic effect becomes pronounced at high initiator concentrations and low reaction temperatures. It is generally believed that the rapid rate increase is due to the formation of precipitated polymeric phase where radical occlusion occurs. The reduced radical mobility in the interior of the particles reduce chain termination rate. The degree of radical occlusion is largest for glassy polymers like polyacrylonitrile which are not highly swollen by the monomer. The degree of occlusion decreases with chain transfer to the monomer or transfer agent and if the reaction temperature is higher than the glass transition temperature of the monomer-polymer mixture [55]. Figure 13 shows the typical polymerization rate curve [56]. Notice that the initial rate acceleration period is followed by an almost constant rate period. Then, the rate increases rapidly to a maximum before

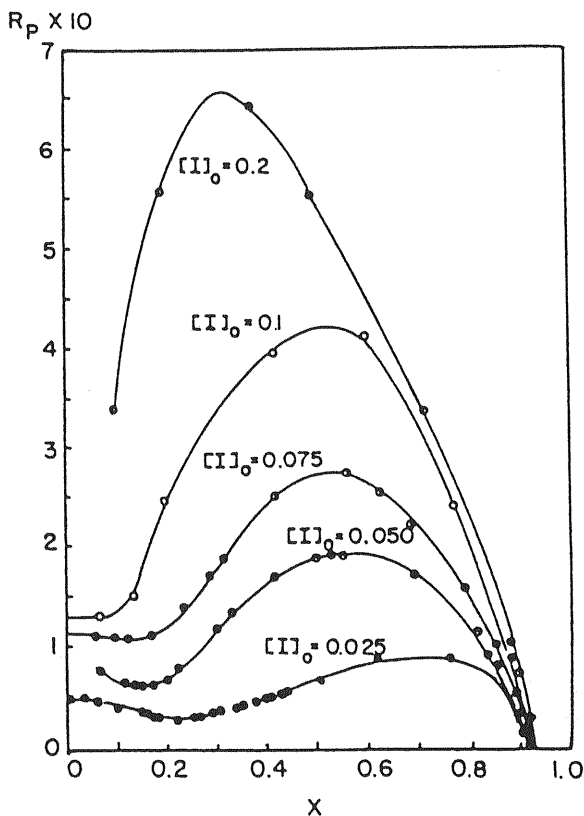


Figure 13 Polymerization rate curves for bulk polymerization of acrylonitrile (60°C with AIBN initiator). (From Ref. 56.)

falling to a zero reaction rate. The polymer molecular-weight averages increase with conversion. The removal of polymerization heat becomes a critical factor in operating a polymerization reactor. Extensive kinetic study and process modeling have been reported in the literature [56,57].

Polyacrylonitrile can be produced by continuous bulk, continuous slurry, and emulsion polymerization processes. In a continuous slurry process, small monomer droplets are suspended in an aqueous medium. In this process, heat removal is more efficient than in the bulk process. In one example [58], a 0.3% H_2SO_4 aqueous solution, a catalyst solution (15% Na_2SO_3 and 4.22% NaClO_3 in water), and a monomer solution are continuously supplied into an agitated reactor. At 35°C, 90% monomer conversion is achieved at 1.7 hr of residence time. A portion of the polymerizing mixture

is circulated from the bottom of the reactor through an external heat exchanger to remove the heat of polymerization.

In the emulsion polymerization process, redox catalyst is commonly used to achieve a rapid polymerization at low temperatures (20–60°C). The polymer is recovered by coagulation with a salt. Acrylonitrile can also be polymerized by solution process with dimethylformamide as a solvent.

VI. POLY(VINYL CHLORIDE)

Poly(vinyl chloride) (PVC) is one of the oldest yet most important thermoplastic polymers. Commercially, PVC is manufactured by three main processes: suspension, mass, and emulsion polymerization. The polymers produced by mass and suspension processes are similar and are used in similar applications. The suspension process is currently the dominating industrial PVC process (about 75% of the world's PVC capacity). The emulsion polymerization process is used to produce specialty resins for paste applications (e.g., coated fabric, roto-molding, slush molding). PVC manufactured by the mass process have properties similar to those of the suspension process.

As PVC is insoluble in vinyl chloride monomer (VCM), the polymerization is a heterogeneous process. The polymer phase separates from the monomer phase at a conversion of 0.1% and the polymerization occurs in both the monomer phase and the polymer phase. It has been suggested that the radicals and polymer formed in each phase grow and terminate without any transfer of active radicals between the phases [59]. Also suggested is that radical transfer occurs between the phases by a sorption and desorption phenomena [60]. It is believed that the monomer phase contains only trace amounts of polymer due to its insolubility in the monomer. The polymer-rich phase is at equilibrium with the monomer as long as there is a free-monomer phase. Thus, for the monomer conversion up to about 77%, the polymer phase separates from the monomer and forms a series of agglomerated polymer particles. The volume of the monomer phase decreases as the polymer phase grows and absorbs the monomer. As the free-monomer phase disappears, the reactor pressure starts to drop. At a higher conversion, the monomer in the polymer-rich phase continues to polymerize.

The most prominent feature of the PVC process is the development of a complex particle morphology. Thus, it is necessary to understand the mechanism of particle nucleation, growth, and aggregation. The mechanism of PVC grains can be summarized as follows [61]:

Stage 1: Primary radicals are formed by the decomposition of initiator.

Macroradicals with a chain length of more than 10–30 monomer

units precipitate from the monomer phase (at $\approx 0.001\%$ conversion). The reaction mixture consists mainly of a pure monomer.

Stage 2: Microdomains ($0.10\text{--}0.02\text{ }\mu\text{m}$, $<0.01\%$ conversion) are produced by the aggregation of precipitated macroradicals and macromolecules.

Stage 3: Aggregation of microdomains produces domains ($0.1\text{--}0.3\text{ }\mu\text{m}$, $<1\%$ conversion; primary particle nuclei) stabilized by negative charge. The limiting size of a domain depends on the agitation speed and additives used. The new domains continue to be formed. This stage is completed at $5\text{--}10\%$ conversion.

Stage 4: Primary particles formed by the aggregation and growth of domains. Primary particles grow with conversion at almost the same rate. The diameter of the spherical particles is about $0.8\text{--}1.0\text{ }\mu\text{m}$. The growth process continues until the formation of a continuous network in droplets (about $15\text{--}30\%$ conversion).

Stage 5: Primary articles grow and aggregate until the free-monomer phase disappears. The diameter of the final primary particles is about $1.2\text{--}1.5\text{ }\mu\text{m}$ ($50\text{--}70\%$ conversion). As the monomer phase disappears, the reactor pressure starts to decrease.

Stage 6: Primary particles fuse together as agglomerates ($5\text{--}10\text{ }\mu\text{m}$) until final conversion is reached.

There is no clear boundary line between stages, and two neighboring stages may occur simultaneously during polymerization. The mechanism of morphology development is illustrated in Fig. 14 [62].

The kinetics of vinyl chloride polymerization are very complex as illustrated as follows [61]:

Initiation	$I \rightarrow 2R^{\bullet}$
Propagation	
Head-to-tail propagation	$P_n^{\bullet} + M \rightarrow P_{n+1}^{\bullet}$
Head-to-head propagation	$P_n^{\bullet} + M \rightarrow P_{n+1}^{*}$
Chlorine shift reaction	$P_n^{*} \rightarrow (P_n^{*})'$
Tail-to-tail propagation	$P_n^{*} + M \rightarrow P_{n+1}^{\bullet}$
Formation of chloromethyl branches	$(P_n^{*})' + M \rightarrow P_{n+1}^{\bullet}$
Splitting off chlorine radical	$(P_n^{*})' \rightarrow M_n + Cl^{\bullet}$
Initiation of polymer radicals by chlorine radical	$Cl^{\bullet} + M \rightarrow P_1^{\bullet}$
Chlorine radical transfer to polymer	$P_n^{\bullet} + Cl^{\bullet} \rightarrow P_n' + HCl$
Propagation toward formation of a chain branch	$P_n^{\bullet} + M \rightarrow P_{n+1}^{\bullet}$

Formation of an internal double bond	$P_n \rightarrow M_n + Cl\cdot$
Chain transfer to polymer	$P_n + M_m \rightarrow M_n' + P_m'$
Formation of long-chain branch	$P_n + M \rightarrow P_{n+1}$
Termination	
Combination	$P_n' + P_m' \rightarrow M_{n+m}$
Disproportionation	$P_n' + P_m' \rightarrow M_n + M_m$
Primary radical termination	$P_n' + R' \rightarrow M_n$
Termination with $Cl\cdot$	$P_n' + Cl\cdot \rightarrow M_n$

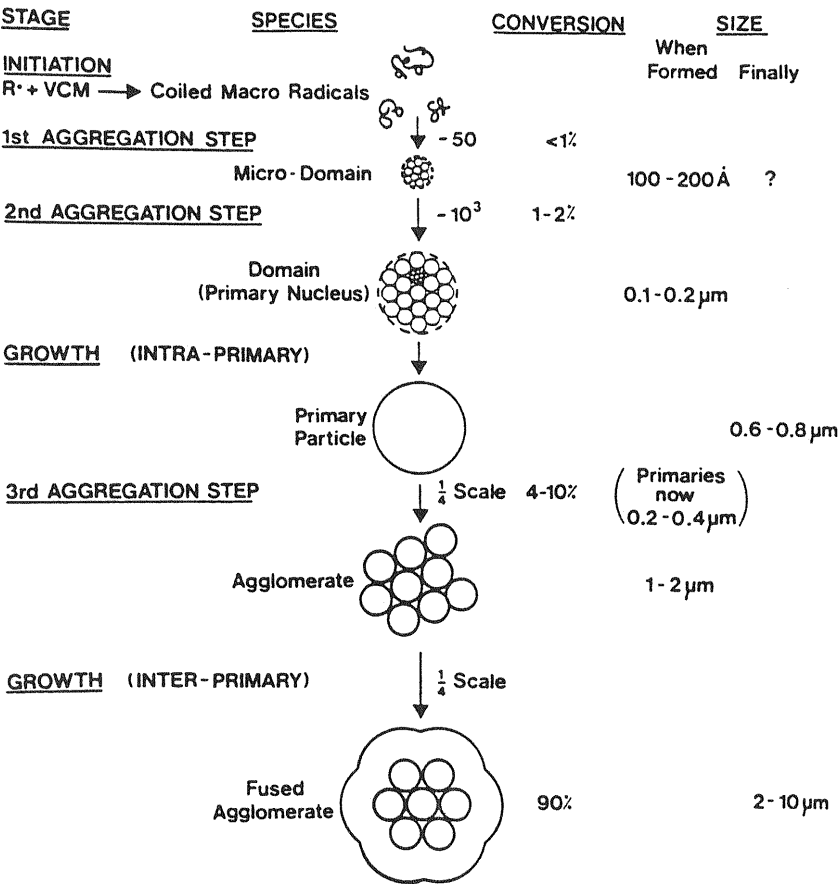
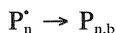
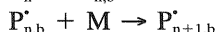


Figure 14 Development of PVC particle morphology. (From Ref. 62.)

Other reactions

Backbiting reaction

Propagation toward formation of
a short branch

As illustrated above, some side reactions occur in vinyl chloride polymerization due to rearrangement effects in the polymer chains, unsaturated structures in the polymer chains (1.5–3.0 double bonds per 1000 monomer units), and the tertiary chlorine structures formed by chain transfer to polymer. The chlorobutyl groups (2–3 per 1000 monomer units) formed by backbiting reactions contribute to the thermal instability of the polymer through the tertiary chlorine on the backbone [63].

The polymer properties to be controlled in commercial PVC manufacturing processes are molecular weight, grain size and its distribution, grain porosity, density, purity, color and thermal stability, and electrical resistivity. Common PVC grades contain 2–3 pendant chloromethyl groups and about 0.5 long branches, formed via hydrogen abstraction from the polymer, per 1000 carbon atoms [64]. Due to the heterophasic nature of PVC polymerization processes, the development of grain morphology is very complex. The kinetics of vinyl chloride polymerization have been reviewed by several authors [61,65].

A. Suspension Polymerization

Suspension polymerization of vinyl chloride (VCM) is carried out in a stirred batch reactor using one or several monomer-soluble organic initiators (e.g., peresters, peroxydicarbonates, peroxides, azo compounds). Initiators are chosen to have decomposition rates that produce polymerization rates to match reactor heat removal capabilities. The monomer is dispersed by agitation in droplets of 50–250 μm and each monomer droplet acts like a microbulk polymerization reactor. One or more protective colloids (or suspension stabilizers) such as a modified cellulose or a partially hydrolyzed polyvinyl acetate (PVA) are added to prevent particle agglomeration and to control the size and morphology of polymer particles. A typical recipe for suspension polymerization is presented in Table 6 [66]. Buffers, chain transfer agents, or comonomers can be added if required. Final PVC grains are about 100–180 μm in diameter. Each PVC grain consists of an agglomerate of a number of smaller grains. Each agglomerate consists of a large number of smaller PVC particles (3–5 μm) that are aggregated into a porous network. The PVC grain is surrounded by a wall or skin approximately 2 μm thick at low conversion. This well-defined membrane or skin has been shown to be a PVA/PVC graft copolymer [67]. At about 30% conversion, the skin is quite strong and stable. During this time, the polymer density changes.

Table 6 Typical Recipe for Suspension Polymerization

Ingredient	VCM (wt%)
Water	100–130
VCM	100
Suspension stabilizer	0.05–0.15
Initiator	0.03–0.07

In a typical commercial PVC suspension process, polymerization begins with the addition of water, suspending agent and initiator to an air-free reactor. Then, the reactor is evacuated to remove oxygen and then VCM is added to the agitated mixture. Agitation is the primary reactor design variable affecting product quality. The mixing blades are usually either retreat curve or turbine types that pump the slurry from the bottom of the reactor upward around the sides of the reactor. Reactors are usually baffled. It is generally known that the product particle size and distribution is established early in the reaction.

Initially, hot water or steam is circulated through the reactor jacket to rapidly bring the reactor contents to the desired temperature. As the reaction heat is released, cooling water is circulated through the jacket to control the reactor temperature. A reflux condenser may be used to improve the reactor's heat removal capability. It is desirable to have a constant rate of polymerization and, thus, a constant rate of heat generation. A mixture of initiators having different decomposition characteristics may be used to keep constant rate of heat release. The effectiveness of the initiator depends on its ability to generate active radicals in the monomer-swollen polymer phase. Any side reaction that removes the initiator from the reaction site will reduce the initiator's effectiveness and may lead to increased fouling [63]. Constant temperature is maintained until 85–90% conversion is obtained. Around 65–70% conversion, most of the unreacted monomer is imbibed in the polymer, and as polymerization proceeds, the pressure within the grain falls and the grain collapses with folding and rupturing of the surface, accompanied by intrusion of water.

Because small polymer particles are produced, fouling of the reactor surface must be minimized. When the fouling occurs, the heat transfer coefficient for the cooling surfaces decreases and the reactor temperature control becomes difficult. Furthermore, the deposits are peeled off from the inner surface of the reactor and mixed into the polymer. As a result, the quality

of the product deteriorates. Figure 15 illustrates the variations in the jacket heat transfer coefficient with conversion [68]. Notice that the jacket heat transfer coefficient decreases rapidly as the monomer conversion approaches 60%. The decrease of the heat transfer coefficient depends on the slurry concentration.

To prevent wall fouling, the following approaches can be taken [63]: prevent the deformation of the monomer droplet; prevent the adhesion of the polymer particles to a reactor surface; prevent the adsorption of monomer to a reactor surface and the polymerization either at the wall or in the aqueous solution. For example, the fouling at the reactor walls can be reduced by using glass-coated reactors, reactor internals with smooth surfaces, fouling suppressants, correct choice of initiator, buffer, and pH. A reflux condenser may be installed to aid the reactor's heat removal capacity. After polymerization, the polymer is steam-stripped to remove residual monomer

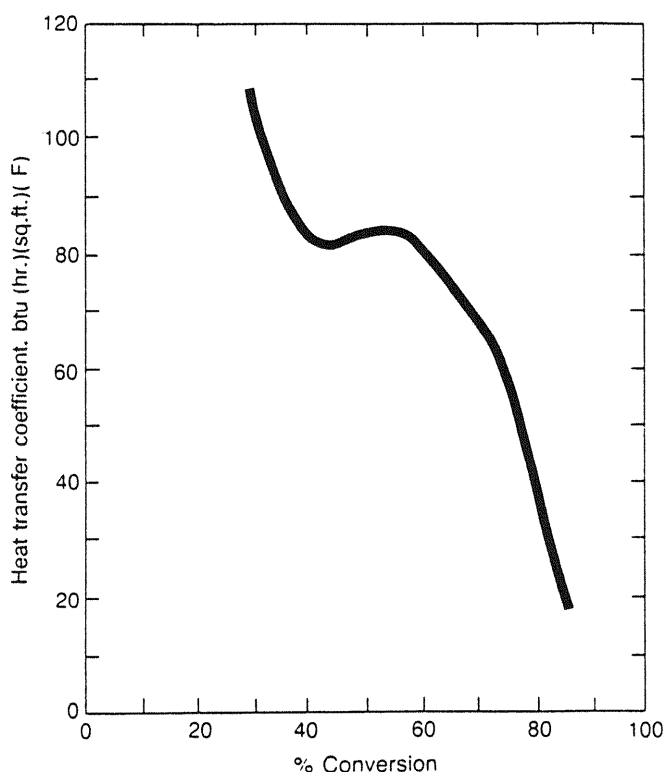


Figure 15 Reactor heat transfer coefficient versus conversion. (From Ref. 68.)

and then dried. Continuous stripping can be done in a trayed stripping tower using steam to heat and strip the slurry. For the drying of PVC particles, fluidized-bed dryers, rotary and flash-fluid-bed dryers are used. In a rotary dryer, concurrent flow of drying air and wet cake is used. A flash-fluid-bed dryer is a two-stage dryer that uses a high-temperature air stream to entrain the wet cake in a duct and dry it through the constant rate section [68]. In a PVC process, high monomer conversion is required to achieve high productivity, and polymer morphology must be properly controlled (e.g., particle shape, size and its distribution, surface characteristics, internal structure, porosity, and bulk density).

In suspension polymerization, the size and size distribution of polymer particles depend on the agitation speed and surface stabilizer. As the stirring speed is increased, the monomer droplets become smaller and the droplet size distribution becomes narrower. If the stirring speed is too high, the droplet size increases. The use of stabilizer yields smaller particles and narrower particle size distribution. The colloidal stability of domains is reduced and earlier aggregation occurs as the polymerization temperature is increased. The size of the primary particles increases and the number decreases, less able to resist droplet contraction, and, consequently, grains with lower porosity are produced [2,69]. The high porosity of the PVC particles leads to the rapid absorption of the additives (e.g., plasticizers). In a typical PVC sample, 1 particle in about 10^5 particles will have a low porosity and a slow rate of plasticizer adsorption. These particles of low porosity may cause the formation of "fish eyes" in a flexible film. A uniformly porous polymer is also desired for ease of VCM removal and processing. Large gels, if present, make the VCM removal difficult and may cause nonuniformity in the final product. Polymer grains with a higher packing density and lower porosity are used in rigid applications to maximize extruder outputs.

Unreacted monomer is removed by evacuation and the polymer recovered from the water slurry. The polymer slurry is centrifuged to produce a wet cake having a water content of 18–25%. A two-stage fluidized bed may be used to dry the polymer to below 0.3 wt% water content [68] by centrifuging and drying. The residual monomer concentration is reduced to less than 10 ppm. The total cycle takes approximately 7–10 hr. The polymerization time is limited by the reactor's heat removal capabilities and by the rate of reaction heat release.

B. Mass Polymerization

In the mass polymerization process, no water is used as in suspension processes. Therefore, in general, the mass polymerization reactor is smaller than

the suspension polymerization reactor. As PVC is insoluble in its own monomer, polymer starts to precipitate from the liquid and the medium becomes opaque as soon as the reaction commences. As soon as the polymer chains start growing, they make up small primary particles about $0.1\text{ }\mu\text{m}$ in diameter. These particles then coagulate to form larger polymer grains which continue to grow during polymerization. Stirring has a strong effect on the formation of polymer grains. At a high stirring speed, no new polymer particle is formed as the conversion reaches about 2%. As the polymerization proceeds, the liquid monomer is absorbed by PVC particles, and at about 30% conversion, the medium becomes powdery.

The PVC grains produced by suspension and mass processes are generally different in shape. In the suspension process, the polymer particle morphology is determined primarily by the interaction between the primary and secondary suspending agents. In the mass process, the particle morphology is controlled by the temperature and agitation in the reactors and by the effects of additives in the first-stage reactor [63]. Figures 16 and 17 illustrate the PVC particles made by two different processes. For a given resin density, PVC made by the mass process exhibits larger porosity. Figure

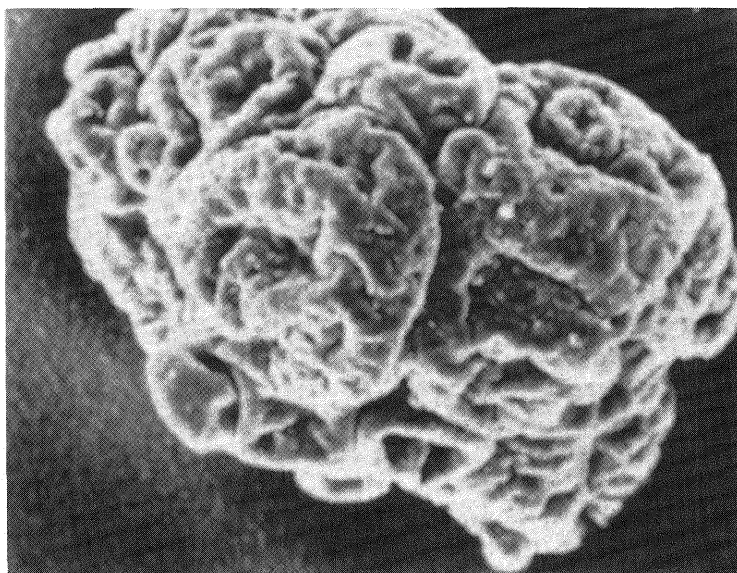


Figure 16 PVC grain by mass process. (From Ref. 69.)

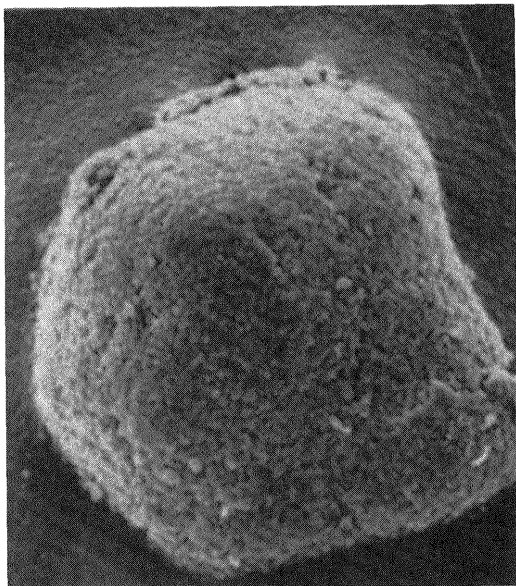


Figure 17 PVC grain by suspension process. (From Ref. 69.)

18 compares the porosity and density of mass and suspension PVC products [69].

Industrial mass PVC processes were developed by many companies. Because mass polymerization begins in a liquid phase and progresses rapidly to a final powder phase, stirring devices must be specially designed to fit such conditions. In a two-step process, each phase of the process is dealt with in a separate reactor. In the first step, prepolymerization is carried out in a stirred tank reactor fitted with a turbine agitator with flat vertical blades and baffles. The prepolymerization reactor is loaded with a mixture of fresh and recycled monomers (about 50% of the total monomer to be polymerized), initiator, and any additives required. The reactor is heated to the pre-specified reaction temperature. Particle size is homogeneous and becomes smaller with more vigorous agitation. When the conversion reaches about 7–8%, particle nucleation is completed. These polymer particles are cohesive enough to allow the transfer of the entire contents of the reactor to a second-stage reactor, where polymerization is finished. In the second-stage reactor, as the conversion exceeds 25% the medium becomes powdery. The second reactor is typically a vertical or a horizontal reactor specially de-

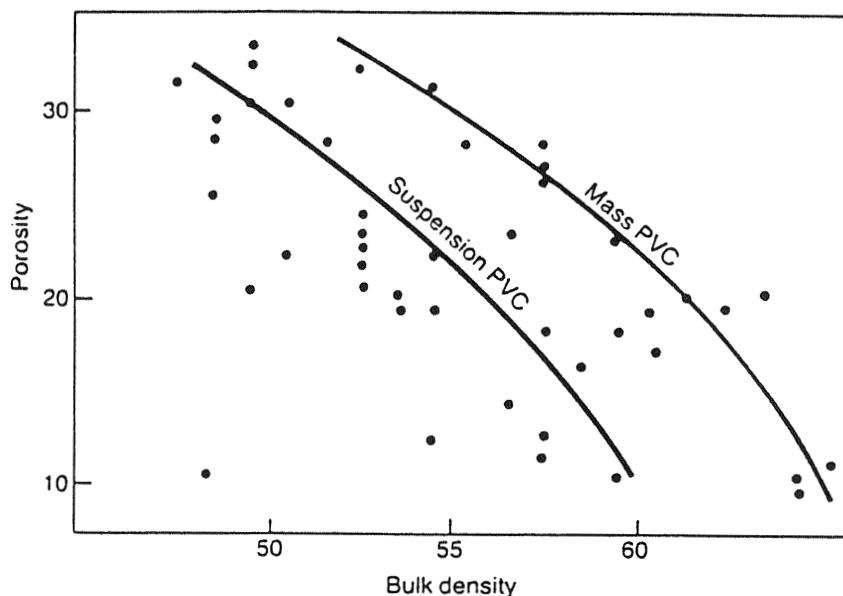


Figure 18 Relationship between porosity and density for mass and suspension PVC. (From Ref. 69.)

signed to stir the powder phase at low speed. Vertical reactors have several advantages: The reactor content can be emptied more rapidly; the reactor can be cleaned more quickly; the reactor temperature can be measured more readily. In practice, only half the total monomer is added in the prepolymerizer and the rest is added in the second reactor.

The mass polymerization is carried out at 40–70°C and 70–170 psi, and the monomer is in equilibrium with the vapor phase. The reaction temperature is kept constant by maintaining constant reactor pressure. It is necessary to have enough monomer to permit the heat transfer by vaporization and a free surface (reactor walls, agitators, condensers) for the recondensation of the monomer. The condensed monomer is readsorbed immediately by the PVC particles because, unlike the suspension process, there is no colloidal membrane (“skin”) around the particle. The residual monomer is degassed directly in the polymerization reactor until equilibrium between the reactor pressure and the pressure of the recovery condenser is achieved. Compressor degassing is then followed until a high vacuum is reached in the reactor (around 100 mm Hg). Finally, the vacuum is broken with nitrogen or water vapor.

C. Emulsion Polymerization

Emulsion polymerization of vinyl chloride is initiated by a water-soluble initiator such as potassium persulfate. Initially in the reactor, monomer droplets are dispersed in the aqueous phase (continuous phase) containing initiator and surfactant (emulsifier). As the reactor content is heated, the initiator decomposes into free radicals. When the surfactant concentration exceeds the critical micelle concentration (CMC), micelles are formed. Free radicals or oligomers formed in the aqueous phase are then captured by these micelles. Vinyl chloride monomer is slightly soluble in water. As the monomer dissolved in water diffuses into micelles containing radicals, polymerization occurs. With an increase in monomer conversion in the polymer particles, separate monomer droplets become smaller and eventually they disappear. The monomer concentration in polymer particles is constant as long as liquid monomer droplets exist. The rate of emulsion polymerization is represented by

$$R_p = \frac{k_p[M]_p \bar{n} N_p}{N_A} \quad (10)$$

where $[M]_p$ is the monomer concentration in a polymer particle, \bar{n} is the average number of radicals per particle, N_p is the number of polymer particles, and N_A is Avogadro's number.

The formation of primary radicals governs the rate of initiation and particle population. Because radical generation occurs in the aqueous phase, whereas radical termination occurs in the polymer particles, the polymerization rate and molecular weight can be increased at the same time. In vinyl chloride emulsion polymerization, the emulsifier greatly affects the polymerization kinetics and the physicochemical and colloidal properties of the polymer. The average polymer particle size is of the order 0.1–0.3 μm , which is the size of primary particle nuclei in bulk and suspension polymerizations. The following is a summary of the typical kinetic features of batch vinyl chloride emulsion polymerization [61]:

- (i) The number of latex particles is independent of the initiator concentration.
- (ii) The number of latex particles varies strongly with the emulsifier concentration.
- (ii) The number of latex particles become constant after 5–10% conversion.
- (iv) The rate of polymerization increases with increasing initiator concentration and the reaction order of initiator varies between 0.5 and 0.8.
- (v) The average number of radicals per particle is less than 0.5 and usually of the order of 0.01–0.001 (Smith–Ewart Case I kinetic).

ics), indicating that radical desorption from polymer particles into the water phase is significant.

- (vi) At high conversion, autoacceleration (Trommsdorf effect) occurs.
- (vii) The polymer molecular weight is independent of particle number and size and initiator concentration.

The emulsion latex, at about 45% solids from the batch stripper, is processed through a thin-film evaporator to increase the latex solids to about 60–65%. Then, the latex is spray-dried and aggregated to about 20–50 μm dry particles.

VII. POLYVINYL ACETATE

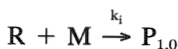
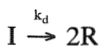
The poly(vinyl acetate (PVAc) homopolymer ($-\text{[CH}_2\text{CH(C(=O)CH}_3\text{)]}-$) is manufactured by polymerizing vinyl acetate (VA) using organic initiators in an alcohol, ester, or aromatic solvents. Redox polymerization of vinyl acetate is industrially used for emulsion polymerization. With a redox system, the activation energy of polymerization is greatly reduced and, thus, low-temperature polymerization becomes possible. Examples of redox initiator systems are hydrogen (activated) with peroxide, hydrogen, and palladiumsol with peroxide, sodium perchlorate (sodium sulfite), peroxides and organic-metal salts, peroxide and titanium sulfate, metal salt–sulfuric acid–benzoyl peroxide, *p*-chlorosulfuric acid–aminebenzoyl peroxide, azobisisobutyronitrile–*p*-chlorobenzene sulfuric acid, and so on [70]. By hydrolysis or alcoholysis, PVAc is converted to poly(vinyl alcohol) (PVA). Vinyl acetate is also used as comonomer for ethylene and vinyl chloride polymerizations.

Industrially, vinyl acetate is polymerized by emulsion, suspension, and solution polymerizations. Due to high exothermicity and the occurrence of branching at a high polymer/monomer ratio, bulk polymerization is not important industrially. As the rate constant of chain transfer to polymer in vinyl acetate polymerization is larger than that in other vinyl polymerization, branching of PVAc is of great practical importance. The chain transfer to polymer occurs mainly on hydrogen atoms of the acetyl group, because the radical so formed is stabilized by the neighboring carbonyl group. The properties of poly(vinyl alcohol) derived from PVAc are also strongly affected by branching. In vinyl acetate polymerization, branch points are introduced in polymer molecules by reaction of polymer radicals with dead polymers and by terminal double bond polymerization. The chain branching exerts a strong influence on the molecular-weight distribution of polymer. The high reactivity of PVAc polymer radical is attributed to its low degree of resonance

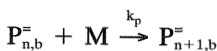
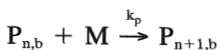
stabilization. It has been reported that branching reactions are highly sensitive to reactor residence time distribution and mixing effects [71]. The polymer molecular weight increases with conversion in bulk vinyl acetate polymerization, whereas the molecular weight of the corresponding poly(vinyl alcohol) remains unchanged with conversion. This indicates that the branching occurs exclusively at the acetoxy group of poly(vinyl acetate) [72]. It was also reported that the hydrogen atoms in the α position of the main polymer chain are more reactive than those on the acetoxymethyl group.

A kinetic scheme for vinyl acetate polymerization can be described as follows [71]:

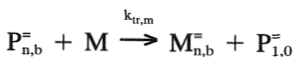
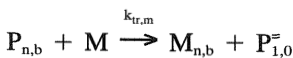
Initiation



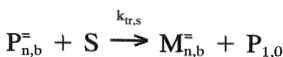
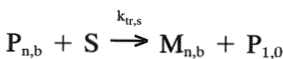
Propagation



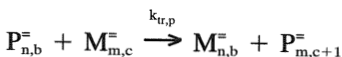
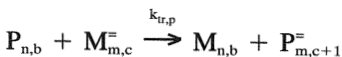
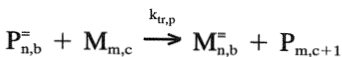
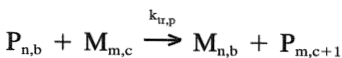
Chain transfer to monomer



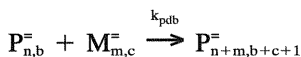
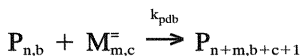
Chain transfer to solvent



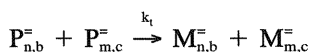
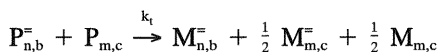
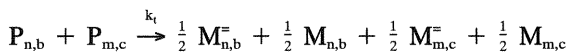
Chain transfer to polymer



Terminal double bond polymerization



Termination by disproportionation



In the above, I is the initiator, R is the primary radical, $P_{n,b}$ is the live polymer radical with n monomer units and b branches, $M_{n,b}$ is the dead polymer with n monomer units and b branches, $P_{n,b}^{\equiv}$ is the live polymer radical with n monomer units, b branches, and a terminal double bond, $M_{n,b}^{\equiv}$ is the dead polymer with n monomer units, b branches, and a terminal double bond, M is the monomer, and S is the solvent.

The above kinetic model allows the calculation of monomer conversion, polymer molecular weight, and branching frequency. The effects of polymerization conditions and the reactor types (e.g., batch, continuous segregated, and continuous micromixed reactors) have been investigated using the above kinetic model [71].

The overall branching density (number of branches per monomer molecule polymerized) can be calculated using the following method. Let N_0 be the total number of monomer molecules (both polymerized and unpolymerized) and x is the fraction of monomer molecules polymerized:

$$x \equiv \frac{N_0 - N}{N_0} \quad (11)$$

where N is the number of monomer molecules when the fractional monomer conversion is x. Also define b as the total number of branches. Then,

$$\frac{db}{dt} = k_{tr,p} P N_0 x \quad (12)$$

$$\frac{dx}{dt} = k_p P (1 - x) \quad (13)$$

From these equations, we obtain

$$\frac{db}{dx} = \left(\frac{k_{tr,p}}{k_p} \right) N_0 \frac{x}{1-x} \equiv C_p N_0 \frac{x}{1-x} \quad (14)$$

Upon integration,

$$\rho \equiv \frac{b}{N_0 x} = -C_p \left(1 + \frac{1}{x} \ln(1-x) \right) \quad (15)$$

This equation indicates that branching is negligible at low monomer conversion. For vinyl acetate polymerization, the following equation has also been proposed [73]:

$$n_B = C_p \overline{DP}_B x \quad (16)$$

where n_B is the average number of branches per molecule grafted onto the polymer backbone, C_p is the polymer chain transfer constant, \overline{DP}_B is the average degree of polymerization of the polymer backbone, and x is the degree of conversion of the monomer. Then, the fraction (F) of the new polymer formed that is grafted to the polymer backbone is given approximately by

$$F = \frac{C_p [B/M]}{C_s ([S]/[M]) + C_m} \quad (17)$$

where $[B/M]$ is the ratio of the weight of the polymer to the weight of the monomer, $[S]/[M]$ is the ratio of the moles of solvent to the moles of monomer, C_s is the solvent chain transfer constant, and C_m is the monomer chain transfer constant. Figure 19 shows the variation of number of branch points

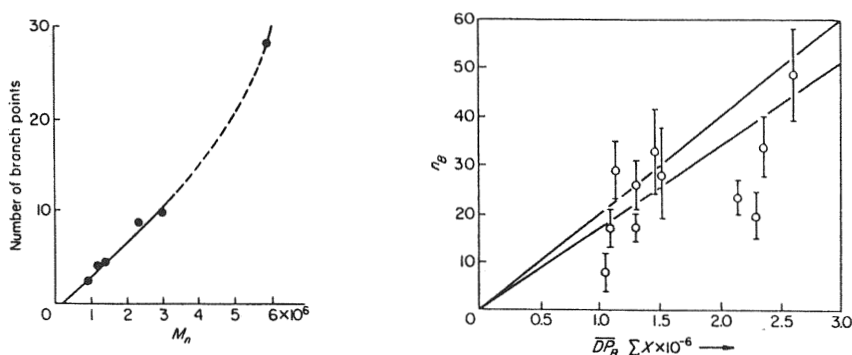


Figure 19 Effect of molecular weight and conversion on branching. (From Refs. 73 and 74.)

with number-average molecular weight of PVAc [74] and the number of branches per molecule and degree of conversion [73]. When branching occurs, the number-average polymer molecular weight is little affected, but the weight-average molecular weight increases. Therefore, the polydispersity (M_w/M_n) increases (i.e., broadening molecular-weight distribution).

A. Emulsion Polymerization

The emulsion polymerization of vinyl acetate (to homopolymers and copolymers) is industrially most important for the production of latex paints, adhesives, paper coatings, and textile finishes. It has been known that the emulsion polymerization kinetics of vinyl acetate differs from those of styrene or other less water-soluble monomers largely due to the greater water solubility of vinyl acetate (2.85% at 60°C versus 0.054% for styrene). For example, the emulsion polymerization of vinyl acetate does not follow the well-known Smith–Ewart kinetics and the polymerization exhibits a constant reaction rate even after the separate monomer phase disappears. The following observations have been reported for vinyl acetate emulsion polymerization [78]: (a) The polymerization rate is approximately zero order with respect to monomer concentration at least from 20% to 85% conversion; (b) the polymerization rate depends on the particle concentration to about 0.2 power; (c) the polymerization rate depends on the emulsifier concentration with a maximum of 0.25 power; (d) the molecular weights are independent of all variables and mainly depend on the chain transfer to the monomer; (e) in unseeded polymerization, the number of polymer particles is roughly independent of conversion after 30% conversion.

Poly(vinyl acetate) latex can be formed with anionic, cationic, and nonionic surfactants, or protective colloids, or even without added surfactant. The ionic strength of the aqueous phase affects the stability of the polymer particles and the polymerization rate. As the ionic strength is increased, the electrostatic repulsive energy barrier is reduced so that the latex coagulates. The average latex particle sizes of commercially produced PVAc are 0.2–10 μm and the viscosity is in the range 400–5000 $\text{mPa}\cdot\text{s}$ [48]. The commonly used water-soluble initiators are ammonium persulfate, potassium persulfate, hydrogen peroxide, and water-soluble azo compounds. The aqueous phase is usually buffered to pH 4–5 with phosphate or acetate to stabilize the decomposition of initiators and to minimize monomer hydrolysis. During the emulsion polymerization, particle formation continues until about 80% conversion is reached. The latex properties (e.g., viscosity, rheology, and solubility) are strongly affected by the degree of grafting. Continuous reactors are commonly used for the emulsion polymerization of vinyl acetate.

B. Solution Polymerization

Bulk polymerization of vinyl acetate is difficult because removing the heat of polymerization is difficult and the occurrence of branching at high polymer/monomer ratios leads to insolubilization. Thus, solution polymerization is preferred industrially in the manufacture of PVAc for adhesive applications or as an intermediate product for poly(vinyl alcohol) production. In solution polymerization of vinyl acetate, it has been known that the solvent has a strong effect on the final polymer molecular weight and the nature of the polymer end groups. The organic solvents that can be employed in solution polymerization of vinyl acetate include benzene, methanol, ethanol, methyl acetate, ethyl acetate, ketones, *tert*-butanol, and water. Among these, methanol is the preferred solvent because poly(vinyl acetate) prepared in methanol solution is used as intermediate for the production of poly(vinyl alcohol).

C. Suspension Polymerization

The suspension polymerization of vinyl acetate is an important industrial process. In suspension polymerization, organic monomer phase is dispersed as fine droplets in an aqueous media. Each monomer droplet, containing organic initiator, acts like a micropolymerization reactor. Homopolymers of vinyl acetate are readily obtained by suspension polymerization. However, vinyl acetate is moderately soluble in water and, thus, coalescence of the suspended polymer particles may occur unless proper reaction conditions (e.g., initiator concentration, suspending agent, stirring rate, pH) are employed. The optimal pH range of 4–5 should be maintained to prevent the hydrolysis of VA during the polymerization (The hydrolysis leads to the formation of acetaldehyde—a strong chain transfer agent.). The polymer particle size distribution is influenced by the concentration of protective colloid and the agitation and agitator geometry.

VIII. POLY(TETRAFLUOROETHYLENE)

Poly(tetrafluoroethylene) (PTFE) is a straight linear polymer with the formula $-(CF_2CF_2)-$ having strong chemical resistance, heat resistance, low friction coefficient (antistick property), and excellent electrical insulation properties. Teflon is a trade name for homopolymers and copolymers of PTFE and is the largest volume fluoropolymer. This polymer has an extremely high molecular weight (10^6 – 10^7) and its high thermal stability is due to the strong carbon–fluorine bond. The close packing of the fluorine atoms

around the carbon backbone provides a protective shield, making the polymer resistant to corrosion. PTFE is produced in three different forms (granular, fine powder, and aqueous dispersion) by suspension and emulsion polymerization processes [48]. Emulsion polymerization produces the PTFE polymer either as an aqueous dispersion or a fine powder. Although granular PTFE can be molded in various forms, the polymer produced by aqueous dispersion is fabricated by dispersion coating or conversion to powder for paste extrusion. The tetrafluoroethylene (TFE) monomer is obtained by pyrolysis of chlorodifluoromethane and is a colorless, tasteless, odorless, and nontoxic gas with heat of polymerization of -172 kJ mol^{-1} . Homopolymers of TFE and its copolymers can also be prepared in the solid state using actinic radiation as initiator.

In suspension polymerization of TFE, an unstable dispersion is formed in the early stages of polymerization. Without a dispersing agent and vigorous agitation, the polymer coagulates partially. As a result, the polymer is stringy, irregular, and variable in shape. The solid polymer recovered is then ground to appropriate particle sizes.

When TFE is polymerized in an aqueous medium with an initiator and emulsifier, PTFE is obtained in a fine-powder form. TFE monomer gas is supplied to a mechanically agitated reactor containing water, an initiator, an emulsifier, and any comonomer. PTFE is polymerized using a free-radical initiator. Termination is predominantly by coupling (radical combination), and chain transfer is negligible. As a result, PTFE has a very high molecular weight. It is important to prevent premature coagulation, although the final polymer is recovered as fine-powder resin. The thin dispersion rapidly thickens into a gelled matrix and coagulates into a water-repellent agglomeration. Typical polymerization conditions are presented in Table 7.

When TFE is polymerized by suspension polymerization, PTFE granules are obtained. Suspension polymerization is carried out in a batch-agitated reactor with or without a dispersing agent. Vigorous agitation is required to keep the polymer in a partially coagulated state. After polymerization, the polymer is separated from the aqueous medium, dried, and ground to the desired size. Unfortunately, very little has been published

Table 7 Typical Polymerization Conditions

Product form	Pressure (psi)	Temperature (°C)
Fine powder	1000	55–240
Aqueous dispersion	15–500	0–95

in open literature concerning the kinetic aspects of TFE free-radical polymerization.

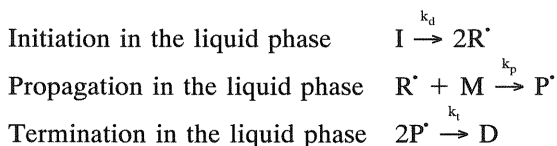
Finely divided powders of PTFE can also be prepared through gamma irradiation of a gaseous TFE monomer.

IX. POLY(VINYL/VINYLDENE CHLORIDE)

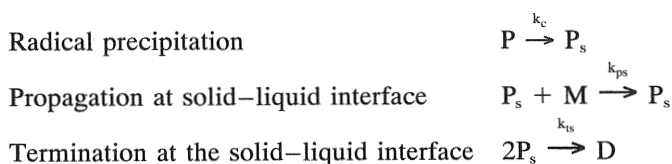
Vinylidene homopolymers and copolymers are known as Saran.* The vinylidene chloride (VDC) monomer ($\text{CH}_2=\text{CCl}_2$) is a colorless liquid with a characteristic sweet odor and soluble in most polar and nonpolar organic solvents. Poly(vinylidene chloride) (PVDC) is a chemical-resistant polymer having high impermeability to gases and vapors. PVDC is highly crystalline in the normal-use temperature range ($0\text{--}100^\circ\text{C}$) because it has a linear symmetrical chain structure which is independent of the polymerization temperature. Thus, PVDC can be oriented into high-strength fibers and films [75]. Due to its extreme thermal instability, PVDC cannot be heated to the molten state for longer than a few seconds without degradation.

Poly(vinylidene chloride) can be polymerized by solution, slurry, suspension, and emulsion processes. Like PVC, PVDC is not soluble in its own monomer. Therefore, when VDC is bulk homopolymerized, the rapid development of turbidity occurs in the reaction medium due to the presence of PVDC crystals at the beginning of polymerization. The heterogeneity of the reaction process exerts a marked influence on the polymerization kinetics. With the progress of reaction to about 20% conversion, it becomes a thick paste. As the conversion increases further, the crystalline phase grows and the liquid slurry becomes a hard, porous solid mass [76]. During the final stage, hot spots can develop in the mass due to the high reaction rate and poor heat transfer. Unlike in the PVC and polyacrylonitrile systems where spherical aggregates are formed, anisotropic growth of polymer particles takes place in the PVDC system.

The following heterogeneous polymerization scheme has been proposed [77]:



*Saran is a registered trademark of the Dow Chemical Co.



where D is the dead polymer.

If the solid polymer phase contains no monomer at high conversion except that adsorbed on its surface, the interior of the polymer crystals should remain inaccessible unless the polymer is heated to a high enough temperature for chain motion in the crystalline phase to occur. Also, if the polymerization occurs only on the solid surface and the radicals precipitate before terminating in the liquid phase, the polymerization rate will increase with conversion because of the increase in surface area. Then, the number of polymer particles, particle shape, and morphology will influence the polymerization kinetics. Assuming that a rectangular lamellar particle grows on the edges only, Wessling proposed the following rate equation [76]:

$$R_p = \left(\frac{f_i k_i k_{ps}^2}{k_{ts}} \right)^{1/2} C_1 [I]_0^{1/2} \left(\frac{N}{M_0} \right)^{1/4} \left(\frac{m}{M_0} \right)^{1/4} \quad (18)$$

where $[I]_0$ is the initiator concentration, M_0 is the number of moles of monomer present initially, m is the number of moles of monomer converted to polymer, N is the number of particles, and C_1 is a morphology factor defined as

$$C_1 = \left[\frac{2d(q+1)}{V_M} \left(\frac{hV_p}{q} \right)^{1/2} \right]^{1/2} \quad (19)$$

q is the ratio of large lamellar dimensions, h is the fold length, d is the thickness of the reaction zone, and V_M is the molar volume.

The PVDC homopolymer is difficult to process. Thus, copolymers of vinylidene chloride-vinyl chloride, vinylidene chloride-alkyl acrylate, vinylidene chloride-acrylonitrile, which are easier to process than PVDC homopolymer, are widely used in industrial processes. The choice of comonomer significantly affects the properties of the copolymer. Table 8 illustrates the reactivity ratios of some important monomers (monomer 1 = VDC) [76].

The introduction of a comonomer such as vinyl chloride into the polymer chains reduces the crystallinity of the polymer to some extent. Practically, amorphous copolymer is obtained with a 3/1 ratio of vinylidene chloride/vinyl chloride mixture [75]. Both emulsion and suspension free-radical polymerization processes are used for commercial production of PVDC co-

Table 8 Reactivity Ratios of Some Important Monomers

Monomer	r_1	r_2
Acrylonitrile	0.49	1.20
Butadiene	<0.05	1.9
Butylacrylate	0.88	0.83
Ethyl vinyl ether	3.2	0.0
Maleic anhydride	9.0	0.0
Methylacrylate	1.0	1.0
Methyl methacrylate	0.24	2.53
Styrene	0.14	2.0
Vinyl acetate	5.0	0.05
Vinyl chloride	3.25	0.3

polymer. Because the vinylidene chloride is easily oxidized, the polymerization is usually carried out at less than 50°C.

When vinyl chloride and vinylidene chloride are copolymerized, the resulting polymer is a heterogeneous mixture of copolymers of different composition due to the large difference between the reactivity ratios of the two monomers ($r_{VC} = 0.3$, $r_{VDC} = 3.2$). To obtain an homogeneous product, the faster-polymerizing monomer should be added during the polymerization to maintain the composition of the monomer mixture constant.

A. Emulsion Polymerization

Emulsion polymerization itself is a heterogenous system. However, in the emulsion polymerization of VDC, polymer precipitates in the latex particles and thus the reaction is also heterogeneous. If the polymer is isolated and used as a dry powder, low soap recipes of marginal colloidal stability are used, whereas if the polymer is to be used as a latex, a higher surfactant concentration is required. PVDC copolymer latex made by the emulsion process are used as a coating compound applied to various substrates. Redox initiator systems are normally used for VDC emulsion polymerization at low temperatures. The emulsion polymerization should be carried out at $\text{pH} < 9$ because the polymer is attacked by an aqueous base [76]. The polymer may be recovered in dry-powder form by coagulating the latex with an electrolyte, followed by washing and drying. A typical recipe for emulsion polymerization is presented in Table 9 [21].

The role of activator is to promote the initiator decomposition so that a lower reaction temperature can be used to obtain a high-molecular-weight

Table 9 Typical Recipe for Emulsion Polymerization

Material	Parts (in wt.)
Vinylidene chloride	78
Vinyl chloride (comonomer)	22
Water	180
Potassium persulfate (initiator)	0.22
Sodium bisulfite (activator)	0.11
Dihexyl sodium sulfosuccinate (emulsifier)	3.58
Nitric acid, 69% (pH control)	0.07

polymer within reasonable reaction times. At 30°C, 95–98% conversion is achieved in a batch reactor after 7–8 hr of reaction time and an average latex particle diameter is 100–150 nm. After polymerization, the emulsion is coagulated, washed, and dried. During the copolymerization in a batch reactor, copolymer composition drift may occur. To prevent it, more reactive monomer or monomer/comonomer mixture may be added into the reactor during the course of polymerization.

To describe the kinetics of VDC emulsion polymerization, the classical Smith–Ewart model and the surface growth model have been used. In the surface growth model, the polymerization is assumed to occur in a restricted zone at the particle surface, not in the core of the polymer particle. The reaction zone can be an adsorbed monomer layer or a highly swollen surface. Then, the particle would grow from the surface outward. Figure 20 illustrates a conversion–time curve for the batch emulsion polymerization of VDC using a Redox initiator system $[(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_5]$ with sodium lauryl sulfate as the emulsifier. Notice that there are three distinct stages [76].

B. Suspension Polymerization

Extrusion- and molding-grade resins of PVDC are manufactured by suspension polymerization at about 60°C to 85–90% conversion for 30–60 hr. Suspension polymers are purer than emulsion polymers; however, polymerization time is significantly longer and a high-molecular-weight copolymer is difficult to obtain. The average size of polymer particles is between 150 and 600 μm. The initiator should be uniformly dissolved in the monomer phase before droplets are formed by mechanical agitation. If initiator distribution is nonuniform, some monomer droplets polymerize faster than others, leading to monomer diffusion from slow-polymerizing droplets to fast-

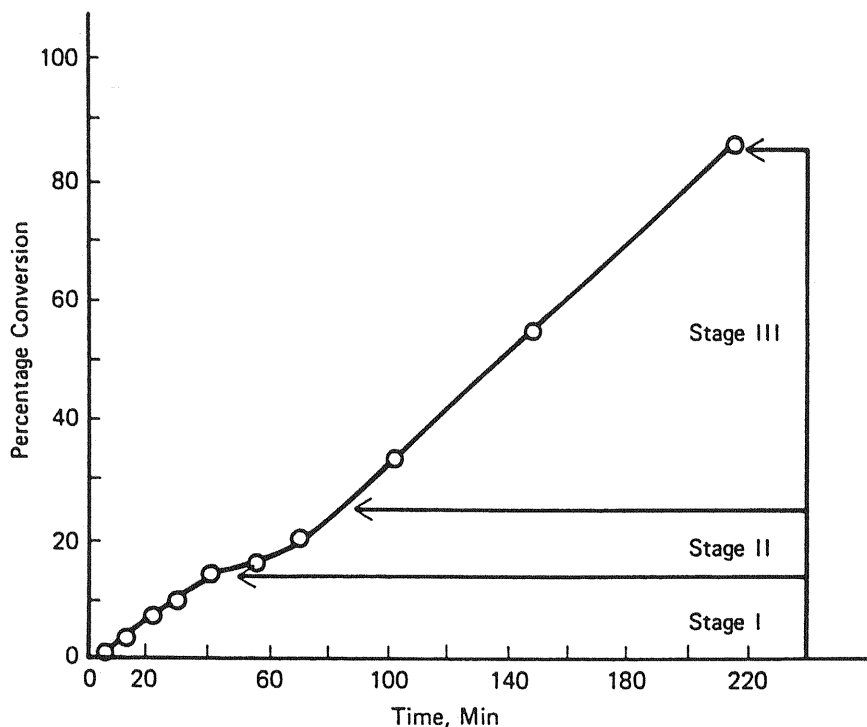


Figure 20 Emulsion polymerization of VDC. (From Ref. 76.)

polymerizing droplets [76]. The fast-polymerizing droplets form dense, hard, glassy polymers that are extremely difficult to fabricate because adding stabilizers or plasticizers is very difficult.

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IV

PARAMETERS

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13

Data and Structures

Yusuf Yagci and Munmaya K. Mishra

Table A Comparison of Polymerization Systems

Type	Advantages	Disadvantages
Homogeneous		
Bulk—batch	Simple equipment	May require solution and subsequent precipitation for purification and/or fabrication May require reduction to usable particle sizes Heat control important Broad molecular-weight distribution
Bulk—continuous	Easier heat control Narrower molecular-weight distribution	Requires reactant recycling May require solution and subsequent ppt. for purification and/or fabrication Requires more complex equipment May require reduction to usable particle size
Solution	Easy agitation May allow longer chains to be formed Easy heat control	Requires some agitation Requires solvent removal and recycling Requires polymer recovery Solvent chain transfer may be harmful (i.e., reaction with solvent)
Heterogeneous		
Emulsion	Easy heat control Easy agitation Latex may be directly usable High polymerization rates possible Molecular-weight control possible Usable, small-particle size possible Usable in producing tacky, soft, and solid products	Polymer may require additional cleanup and purification Difficult to eliminate entrenched coagulants, emulsifiers, surfactants, etc. Often requires rapid agitation

Table A Continued

Type	Advantages	Disadvantages
Precipitation	Molecular weight and molecular-weight distribution controllable by control of polymerization environment	May require solution and reprecipitation of product to remove unwanted material Precipitation may act to limit molecular-weight disallowing formation of ultrahigh-molecular-weight products
Suspension	Easy agitation Higher-purity product when compared to emulsion	Sensitive to agitation Particle size difficult to control

Source: Data compiled from R. B. Seymour and C. E. Carraher, Jr., *Polymer Chemistry*, Marcel Dekker, Inc., New York, 1992.

Table B Physical Properties of Some Common Vinyl Monomers

Monomers	Formula	Molecular weight	Density at 20°C	Boiling point (°C)	Melting point (°C)	Solubility ^a
Acrylaldehyde	$\text{CH}_2=\text{CHCHO}$	56.06	0.8410	52.5	-87	W, A, E
Acrylamide	$\text{CH}_2=\text{CHCONH}_2$	71.08	1.122 ³⁰	125 ²⁵	84.8	W, A, E, C
Acrylic acid	$\text{CH}_2=\text{CHCO}_2\text{H}$	72.06	1.0511	141.3	12.3	
Acrylonitrile	$\text{CH}_2=\text{CHCN}$	53.06	0.8060	77.5	-83	W
Butyl acrylate	$\text{CH}_2=\text{CHCO}_2\text{C}_4\text{H}_9$	128.17	0.8986	69 ⁵⁰	-64.6	A, E
Butyl methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{C}_4\text{H}_9$	142.20	0.8936	165	-76	A, E
<i>p</i> -Chloro styrene	$\text{ClC}_6\text{H}_4\text{CH}=\text{CH}_2$	138.6	1.0868	192	-15.9	A, E, Bz
Ethyl acrylate	$\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$	100.12	0.924	99	-75	
Methacrylic acid	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{H}$	86.09	1.0153	60 ¹²	16	W, A, E
Methacrylonitrile	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$		0.7998	90.3	-36	
Methyl acrylate	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$	86.09	0.9535	79.6	-75	A, E
Methyl methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	100.12	0.9440	100	-48	A, E
α -Methyl styrene	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2$		0.9165 ¹⁰	163.4	-23.2	
Styrene	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	104.15	0.9060	145.2	-30.6	A, E
Vinyl acetate	$\text{CH}_3\text{CO}_2\text{CH}=\text{CH}_2$	86.09	0.9317	72.5	-93.2	A, Bz
Vinyl butyl ether	$\text{CH}_2=\text{CHOC}_4\text{H}_9$	100.16	0.7888	93.8	-112	A, E
Vinyl chloride	$\text{CH}_2=\text{CHCl}$	62.5	0.9106	-13.37	-153.79	A, E
Vinyl ether (divenyl)	$\text{CH}_2=\text{CHOCH}=\text{CH}_2$	70.09	0.773	39	-101	
Vinyl ethyl ether	$\text{C}_2\text{H}_5\text{OCH}=\text{CH}_2$	72.11	0.7589	35	-115	A
Vinyl fluoride	$\text{CH}_2=\text{CHF}$	46.04	—	-72.2	-161	
Vinyl methyl ether	$\text{CH}_3\text{OCH}=\text{CH}_2$	58.08	0.7500	12	-122	A, E

^aW = water; E = ether; A = alcohol; C = chloroform; Bz = benzene.Source: Portions of the data were compiled from J. B. Bandrup and E. H. Immergut, eds., *Polymer Handbook*, 3rd ed., Wiley-Interscience, New York (1989).

Table C Chain Transfer Constants of Solvents to Different Monomers in Free-Radical Chain Polymerization

Monomer	Solvent	Temp (°C)	Cs $\times 10^4$	Ref. ^a
Acrylamide	Methanol	30	0.13	1
	Water	40	5.8	2
Acrylic acid, ethyl ester	Cyclohexane	50	28.9	3
		60	0.48	3
	Hexane	50	0.524	3
		60	0.593	3
	Toluene	50	0.611	4
		60	0.929	4
Acrylic acid, methyl ester	Benzene	80	0.326	5
	Toluene	60	2.7	6, 7
		80	1.775	5
	CCl ₄	40	1.0	8
Acrylonitrile	Acetone	50	1.7	9
	Benzene	60	2.46	10
	CCl ₄	60	0.85	11
	Chloroform	60	5.64	10
	Toluene	50	1.153	12
		60	2.632	12
Methacrylic acid, ethyl ester	Benzene	80	0.081	13
	CCl ₄	60	0.901	13
	Chloroform	60	0.703	13
	Ethyl acetate	80	0.919	13
	Heptane	80	0.865	13
	Toluene	80	0.436	13
Methyl methacrylate	Acetone	60	0.195	14
		80	0.225	15
	Benzene	50	0.036	16, 17
		60	0.040	14
	CCl ₄	50	0.82	18
		60	0.925	14
		80	2.393	15
		60	0.454	14
	Chloroform	80	1.124	14
	Cyclohexane	60	12.0	19
		80	0.1	15
	<i>p</i> -Dioxane	80	0.222	15
	Ethyl acetate	60	0.100	20
	Heptane	50	1.8	21
	Methanol	60	0.2	22
		80	0.33	22

Table C Continued

Monomer	Solvent	Temp (°C)	Cs $\times 10^4$	Ref. ^a
Styrene	Toluene	60	0.170	6, 14
	Water	60	0	23
	Acetone	60	4.1	24
	Benzene	50	0.01	17
		60	0.018	25
		70	5.5	26
	Butyl alcohol	50	6.5	27
		60	0.06	28
	<i>t</i> -Butyl alcohol	50	6.6	27
		60	0.22	29
	Carbon tetrachloride	60	84	30
		80	133	31
	Chloroform	60	0.5	28, 32
		80	0.916	33
	<i>p</i> -Dioxane	60	2.75	24
	Ethyl acetate	60	15.5	34
		75	6.67	26
	Hexane	100	0.9	35
	Methanol	60	0.296	36
		80	1.10	22
Vinyl acetate	Toluene	60	0.105	37
		80	0.15	38
		100	0.53	39
	Water	60	0.006	36
	Acetone	60	1.5	19
		70	25.6	40
	Benzene	60	1.07	41
		70	5.27	42
		75	1.4	19
	Butyl alcohol	60	20.0	43
		70	29.1	42
	Sec. Butyl alcohol	60	31.74	44
		70	6.21	42
	Carbon tetrachloride	60	800	45
		70	2023	46
	Chloroform	60	130	43
	Cyclohexane	60	6.59	44
	<i>p</i> -Dioxane	60	20	19
		70	49.1	42
	Ethyl acetate	50	2.9	47
		60	1.07	44
		70	7.8	42

Table C Continued

Monomer	Solvent	Temp (°C)	Cs $\times 10^4$	Ref. ^a
	Ethyl alcohol	60	25	19
		70	26.3	42
	Heptane	50	17.0	47
	Methanol	60	2.26	43, 48
		70	5.5	49
	Toluene	50	12.0	50
		60	17.8	51
		70	21.1	51
	Xylene	50	14.9	50
		70	278	42
Vinyl chloride	CCl ₄	60	280	52
	Chloroform	60	290	52

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Source: Portions of the data were compiled from J. B. Bandrup and E. H. Immergut, eds., *Polymer Handbook*, 3rd ed., Wiley-Interscience, New York (1989).

Table D Typical Free-Radical Chain-Copolymerization Reactivity Ratios of Some Selected Monomers at Different Temperatures

Monomer 1	Monomer 2	r_1	r_2	$r_1 r_2$	Temp. (°C)
Acrylamide	Acrylic acid	1.38	0.36	0.5	60
	Acrylonitrile	1.3	0.8	1.04	60
	Methyl acrylate	1.30	0.05	0.07	60
	Vinylidene chloride	4.9	0.15	0.74	60
Acrylic acid	Acrylamide	0.36	1.38	0.5	60
	Acrylonitrile	1.15	0.35	0.40	50
	Methyl methacrylate	0.33	2.17	0.72	50
	Styrene	0.25	0.15	0.04	60
	Vinyl acetate	2.0	0.1	0.2	70
Acrylonitrile	Acrylic acid	0.35	1.15	0.40	50
	Acrylamide	0.8	1.3	1.04	60
	Butadiene	0.02	0.3	0.006	40
	Butadiene	0.25	0.33	0.08	60
	<i>t</i> -Butyl vinyl ether	0.14	0.003	0.0004	60
	Ethyl acrylate	1.17	0.67	0.78	50
	Methyl vinyl ether	0.7	0.03	0.021	80
	Methacrylic acid	0.09	2.5		70
	Methyl acrylate	1.5	0.84	1.26	
	Methyl methacrylate	0.15	1.22	0.183	80
	α -Methyl styrene	0.06	0.1		75
	Methyl vinyl ketone	0.61	1.78	1.0858	60
	Styrene	0.04	0.4	0.016	60
	Vinyl acetate	4.2	0.05	0.21	50
	Vinyl chloride	2.7	0.04	0.11	60
	Vinylidene chloride	0.91	0.37	0.34	60
	2-Vinylpyridine	0.113	0.47	0.05	60
	4-Vinylpyridine	0.11	0.41	0.045	60
Allyl acetate	Methyl methacrylate	0	23	0	60
	Styrene	0	90	0	60
	Vinyl acetate	0.7	1.0	0.7	60
	Acrylonitrile	0.3	0.02	0.006	40
Butadiene	Isoprene	0.75	0.85	0.64	5
	Methacrylonitrile	0.36	0.04	0.014	5
	Methyl methacrylate	0.75	0.25	0.188	90
	Styrene	1.35	0.58	0.78	50
	Vinyl chloride	8.8	0.035	0.31	50
	2-Vinylpyridine	0.94	0.9	0.85	50
Methacrylonitrile	Methyl methacrylate	0.65	0.67	0.44	60
	Styrene	0.32	0.39	0.12	60
	Vinyl acetate	12	0.01	0.12	70

Table D Continued

Monomer 1	Monomer 2	r_1	r_2	r_1r_2	Temp (°C)
Methacrylic acid	Acrylonitrile	2.5	0.09	0.23	70
	Butadiene	0.53	0.20	0.11	50
	Styrene	0.7	0.15	0.11	60
	Vinyl acetate	20	0.01	0.2	70
	Vinyl chloride	36	0.03	1.08	50
	2-Vinylpyridine	0.58	1.55	0.9	70
Methyl acrylate	Acrylamide	0.05	1.3	0.07	60
	Acrylonitrile	0.67	1.26	0.84	60
	Ethyl vinyl ether	3.3	0	0	60
	Methyl methacrylate	0.50	1.91	0.96	130
	Styrene	0.20	0.75	0.15	60
	Vinyl acetate	9	0.1	0.9	60
	Vinyl chloride	4	0.06	0.24	45
	2-Vinylpyridine	0.20	2.03	0.41	60
Methyl methacrylate	4-Vinylpyridine	0.22	1.7	0.37	60
	Methyl acrylate	1.91	0.5	0.96	130
	Methacrylonitrile	0.67	0.65	0.44	60
	Styrene	0.46	0.52	0.24	60
	α-Methyl styrene	0.5	0.14	0.07	60
	Vinyl acetate	20	0.02	0.4	60
	Vinyl chloride	10	0.1	1.0	68
	Vinylidene chloride	2.53	0.24	0.61	60
α-Methyl styrene	Acrylonitrile	0.1	0.06	0.01	75
	Methyl methacrylate	0.14	0.5	0.07	60
	Styrene	0.3	1.3	0.39	60
Methyl vinyl ketone	Styrene	0.35	0.29	0.10	60
	Vinyl acetate	7.0	0.05	0.35	70
	Vinyl chloride	8.3	0.1	0.83	70
	Vinylidene chloride	1.8	0.55	0.99	70
Styrene	<i>p</i> -Chlorostyrene	0.74	1.03	0.76	60
	Methacrylonitrile	0.39	0.32	0.12	60
	Methyl acrylate	0.75	0.20	0.15	60
	Methyl methacrylate	0.52	0.46	0.24	60
	α-Methyl styrene	1.3	0.3	0.39	60
	Methyl vinyl ketone	0.29	0.35	0.10	60
	Ethyl vinyl ether	80	0	0	80
	<i>p</i> -Methoxy styrene	1.16	0.82	0.95	60
	Methacrylic acid	0.15	0.7	0.11	60
	Vinyl acetate	55	0.01	0.55	60
	Vinyl chloride	17	0.02	0.34	60
	Vinylidene chloride	1.85	0.09	0.17	60

Table D Continued

Monomer 1	Monomer 2	r_1	r_2	$r_1 r_2$	Temp. (°C)
Vinyl acetate	2-Vinylpyridine	0.55	1.14	0.63	60
	N-Vinylpyrrolidone	24.2	0.08	1.94	60
	Ethyl vinyl ether	3.0	0	3.0	60
	Methacrylic acid	0.01	20	0.2	70
	Methacrylonitrile	0.01	12	0.12	70
	Vinyl chloride	0.23	1.68	0.39	60
	Methyl acrylate	0.1	9	0.9	60
	Methyl methacrylate	0.02	20	0.4	60
	Vinylidene chloride	0.1	6.0	0.6	68
	Methyl vinyl ketone	0.05	7.0	0.35	70
	Styrene	0.01	55.0	0.55	60
Vinyl chloride	Vinyl laurate	1.4	0.7	0.98	60
	Methyl acrylate	0.06	4	0.24	45
	Methacrylic acid	0.03	36	1.08	50
	Vinylidene chloride	0.3	3.2	0.96	60
	Methyl vinyl ketone	0.1	8.3	0.83	70
N-Vinylpyrrolidone	Styrene	0.05	15.7	0.79	50
	Styrene	0.08	24.2	1.94	60

Source: Portions of the data were compiled from J. B. Bandrup and E. H. Immergut, eds., *Polymer Handbook*, 3rd ed., Wiley-Interscience, New York (1989).

Table E Rate Constants of Some Common Initiators for Vinyl Polymerization

Initiators Solvent	Temp. (°C)	K_d (sec ⁻¹) × 10 ⁸	E_a (kcal mol ⁻¹)	Ref. ^a
AZO COMPOUNDS				
2,2'-Azo-bis-isobutyronitrile				
Benzene	40	54.4	30.7	1
	50	264		1
	60	915		2
	100	152,000		2
Cyclohexane	82	14,300		3, 4
Methyl methacrylate	50	97		5
	70	3,100		6
Styrene	50	297	30.5	7
	70	4,720		7
Toluene	60	903		8
	70	4,000	29.0	9
	100	160,000		9
Ethyl acetate	40	47	30.7	1
	60	936		1
Xylene	50	200		4
	80	15,300	31.3	10
Phenyl-azo-diphenylmethane				
Decalin	125	3,440	34	11
Phenyl-azo-triphenylmethane				
Benzene	25	429	26.8	12
	50	13,700		13
Cyclohexane	25	422	24.5	12
	50	9,900		12
Decane	60	57,200		13
Heptane	60	66,000		13
Hexane	60	76,000		13
Octane	60	64,100		13
Toluene	50	17,300		13
	45	8,480		14
PEROXIDES				
<i>tert</i> -Butyl peroxide				
Benzene	80	7.81	34	15
	100	88	35	16, 17
	120	1,100	35.3	18
	130	3,220		18
Cyclohexane	95	24.8	40.8	19
	120	630		18
	130	2,590		18

Table E Continued

Initiators Solvent	Temp. (°C)	K_d (sec ⁻¹) × 10 ⁸	E_a (kcal mol ⁻¹)	Ref. ^a
Decane	80	1.39		20
	110	201		20
	130	2,480		20
	140	6,660		17
Heptane	80	1.44		20
	110	219		20
Hexane	80	1.64		20
	110	217		20
Octane	80	1.48		20
	110	219		20
Toluene	100	68.2		21
	125	1,600		22
Cumyl peroxide				
Benzene	115	2,050	38	17
Dodecane	128	8,750		23
Acetyl peroxide				
Benzene	50	110	32	17
	60	500		24
	70	2,390		25
Cyclohexane	55	210	31.4	26, 27
	75	3,600		26, 27
Decane	80	6,850		28
Heptane	80	7,720		28
<i>n</i> -Hexane	60	340		29
<i>n</i> -Octane	60	290		29
	80	7,340		28
Toulene	55	270	32	26, 27
	60	500	31	24
	75	4,700		26, 27
	85	15,900		26, 27
Benzoyl peroxide				
Benzene	30	4.8	27.8	30
	60	200	29.7	31
	70	1,170	32	32
	75	1,660	29.7	33
Cyclohexane	80	7,720		34
Decane	80	2,530		20
<i>n</i> -Heptane	80	2,710		20
Hexane	80	2,850		20
Styrene	50	70	30.5	35
	60	270		35
	70	990		35

Table E Continued

Initiators Solvent	Temp. (°C)	K_d (sec ⁻¹) × 10 ⁸	E_a (kcal mol ⁻¹)	Ref. ^a
Toluene	30	4.94	28.8	30
	49	60	29.6	1
	60	224		8
	70	1,100		1
Lauroyl peroxide				
Benzene	30	25.6		36
	40	49.1		37
	50	219		37
	60	1,510	30.4	16, 17
	70	5,580		16, 17
Ethyl acetate	40	60.3		37
	50	270		37
	70	3,990		37
<i>tert</i> -Butyl hydroperoxide				
Benzene	130	30	32.9	17
	154	429	40.8	38
	160	660		17
Cyclohexane	100	12		39
Dodecane	86	132	30.7	40
Heptane	172	14,100		21
<i>n</i> -Octane	150	800	39	41
	160	2,500		41
	170	6,900		41
	180	1,820		41
	100	5.7		39
<i>tert</i> -Butyl peracetate				
Benzene	85	218	36.3	16, 17
	100	1,540		16, 17
Decane	100	1,500	32	17
Hexane	130	50,800		42
Octane	100	2,070		20
<i>tert</i> -Butyl perbenzoate				
Benzene	100	1,070	34.7	16, 17
	110	3,500	34.5	43
	130	33,000		43
Decane	100	1,400	32.0	17
	130	35,600		17
Heptane	115	7,210		20
Octane	115	7,060		20
Xylene	119	10,900	33.8	43
	130	34,200		43

Table E Continued

Initiators Solvent	Temp. (°C)	K_a (sec ⁻¹) × 10 ⁸	E_a (kcal mol ⁻¹)	Ref. ^a
<i>tert</i> -Butyl peroxate				
Benzene	70	1,400	31	17
	100	45,500		17
Decane	70	690	31	17
	100	26,400		17
Potassium persulfate				
0.1 M NaOH	50	950	33.5	44
	70	2,330		44
	90	35,000		44
Water (pH 3)	50	166		44
Water	40	1,650,000	19.9	45
	50	378,000	29	45
	60	2,180,000		45
	70	5,010,000		45
	80	5,780		46

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Table footnotes continued on following page

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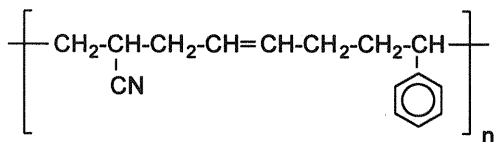
Table F Glass Transition Temperature of Some Common Vinyl Polymers

Polymer	T_g (°C)	T_m (°C)
Poly(acrylic acid)	106	
Poly(butyl acrylate)	-54	
Poly(t-butyl acrylate)	43-107	
Poly(isobutyl acrylate)	-24	
Poly(acrylamide)	165	
Poly(butyl methacrylate)	13-35	
Poly(methacrylic acid)	228	
atactic	105	200
isotactic	38	
syndiotactic	99	
Poly(vinyl fluoride)	-41	200
Poly(vinyl methyl ether)	-31	
Poly(vinyl alcohol)	85	
Poly(acrylonitrile)	125	
Poly(vinyl chloride)	81	
Poly(vinyl acetate)	32	
Poly(4-bromostyrene)	118	
Poly(4-chlorostyrene)	110	
Poly(α -methyl styrene)	20	
Poly(4-methyl styrene)	97	
Poly(styrene)-isotactic and atactic	100	240

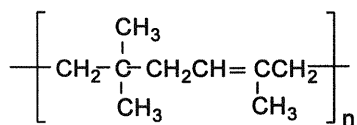
Source: Portions of the data were compiled from J. B. Bandrup and E. H. Immergut, eds., *Polymer Handbook*, 3rd ed., Wiley-Interscience, New York (1989).

Table G Structures of Some Common Vinyl Polymer

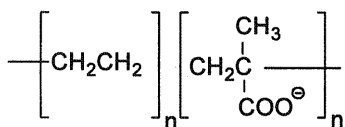
Acrylonitrile-butadiene-styrene terpolymer (ABS)



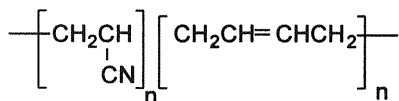
Butyl rubber



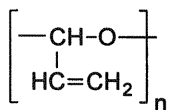
Ethylene-methacrylic acid copolymers (Ionomers)



Nitrile rubber (NBR)



Polyacrolein



Polyacrylamide

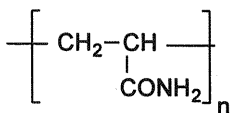
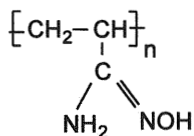
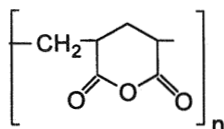


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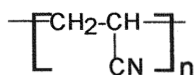
Poly(acrylamide oxime)



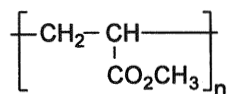
Poly(acrylic anhydride)



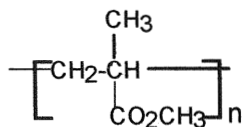
Polyacrylonitrile



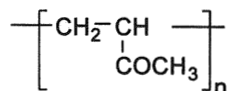
Poly(methyl acrylate)



Poly(methyl methacrylates) (PMMA)



Poly(methyl vinyl ketone)



Polystyrene (PS)

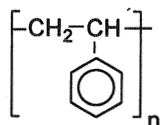
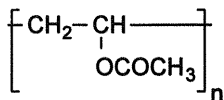
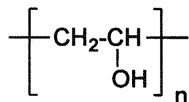


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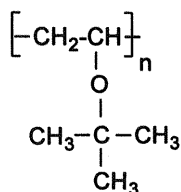
Poly(vinyl acetate)(PVAc)



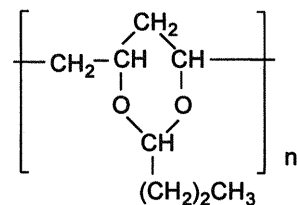
Poly(vinyl alcohol) (PVA)



Poly(vinyl t-butyl ether)



Poly(vinyl butyral) (PVB)



Poly(vinyl butyrate)

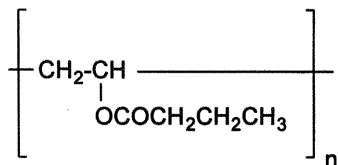
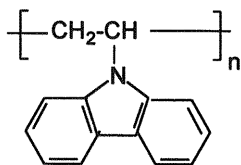
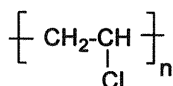


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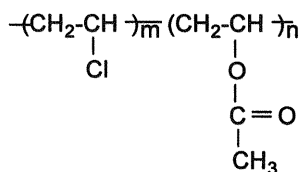
Poly(vinyl carbazole)



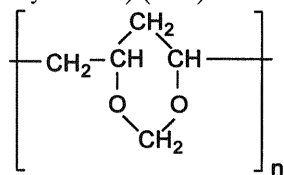
Poly(vinyl chloride) (PVC)



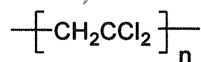
Poly(vinyl chloride-co-vinyl acetate)



Poly(vinyl formal) (PVF)



Poly(vinylidene chloride)



Poly(vinyl isobutyl ether)

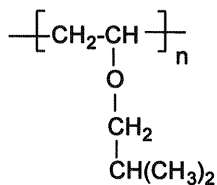
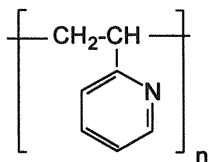
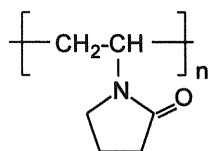


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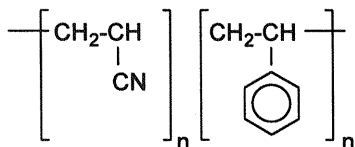
Poly(vinyl pyridine)



Poly(vinyl pyrrolidone)



Styrene-acrylonitrile copolymer (SAN)



Styrene-butadiene rubber (SBR)

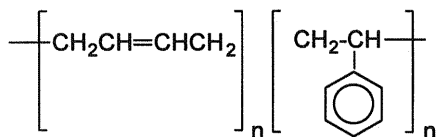


Table H Trade/Brand Name and Manufacturer of Some Selected Vinyl Polymers

Trade or brand name	Product	Manufacturer
Abafil	Reinforced ABS	Rexall Chemical Co.
Absafil	ABS polymers	Fiberfil
Abson	ABS polymers	B. F. Goodrich Chemical Co.
Acralen	Styrene-butadiene latex	Farbenfabriken Bayer AG
Acronal	Polyalkyl vinyl ether	General Aniline Film Corp.
Acrilan	Polyacrylonitrile	Chemstrand Co.
Acrylan-Rubber	Butyl acrylate-acrylonitrile copolymer	Monomer Corp.
Acrylite	Poly(methyl methacrylate)	American Cyanamid Co.
Afcoryl	ABS polymers	Pechiney-Saint-Gobain
Argil	Styrene copolymer monofilament	Shawinigan Chemicals, Ltd.; also Polymer Corp.
Bexone F	Poly(vinyl formal)	British Xylonite
Benvic	Poly(vinyl chloride)	Solvay & Cie S.A.
Bexphane	Polypropylene	Bakelite Xylonite Ltd.
Blendex	ABS resin	Borg-Warner Corp.
Bolta Flex	Vinyl sheeting and film	General Tire & Rubber Co.
Butacite	Poly(vinyl acetal) resins	E. I. du Pont de Nemours Co., Inc.
Butakon	Butadiene copolymers	Imperial Chemical Industries, Ltd.
Butaprene	Styrene-butadiene elastomers	Firestone Tire & Rubber Co.
Butarez CTL	Telechelic butadiene polymer	Phillips Petroleum Co.
Buton	Butadiene-styrene resin	Enjay Chemical Co.
Bu-Tuf	Polybutene	Petrotex Chemical Corp.
Butvar	Poly(vinyl butyral) resin	Shawinigan Resins Corp.
Carina	Poly(vinyl chloride)	Shell Chemical Co. Ltd.
Carinex	Polystyrene	Shell Chemical Co. Ltd.
Celatron	Polystyrene	Celanese Plastics Co.
Cellofoam	Polystyrene foam board	United States Mineral Products Co.
Cerex	Styrene copolymer	Monsanto Chemical Co.
Cobex	Poly(vinyl chloride)	Bakelite Xylonite Ltd.
Cordo	PVC foam and films	Ferro Corp.
Corvic	Vinyl polymers	Imperial Chemical Industries Ltd.
Courlene	Polyethylene (fiber)	Courtaulds
Covol	Poly(vinyl alcohol)	Corn Products Co.
Creslan	Acrylonitrile-acrylic ester copolymers	American Cyanamid Co.
Crystalex	Acrylic resin	Rohm & Haas Co.
Cycolac	Acrylonitrile-butadiene-styrene copolymer	Borg-Warner Corp.
Daran	Poly(vinylidene chloride) emulsion coatings	W. R. Grace & Co.

Table H Continued

Trade or brand name	Product	Manufacturer
Darex	Styrene copolymer resin	W. R. Grace & Co.
Darvan	Poly(vinylidene cyanide)	Celanese Corp. of America
Darvic	Poly(vinyl chloride)	Imperial Chemical Industries, Ltd.
Degalan	Poly(methyl methacrylate)	Degussa
Diakon	Poly(methyl methacrylate)	Imperial Chemical Industries Ltd.
Dralon	Polyacrylonitrile fiber	Farbenfabriken Bayer AG
Dynel	Vinyl chloride-acrylonitrile copolymers	Union Carbide Corp.
Dylel	ABS copolymer	Sinclair-Koppers Co., Inc.
Dylene	Polystyrene resins	ARCO Polymer, Inc.
Dylite	Expandable polystyrene	Sinclair-Koppers Co., Inc.
Ecavyl	Poly(vinyl chloride)	Kuhlmann
Elvacet	Poly(vinyl acetate) emulsion	E. I. du Pont de Nemours & Co., Inc.
Elvacite	Acrylic resins	E. I. du Pont de Nemours & Co., Inc.
Elvanol	Poly(vinyl alcohol) resins	E. I. du Pont de Nemours & Co., Inc.
Elvax	Poly(ethylene-co-vinyl acetate)	E. I. du Pont de Nemours & Co., Inc.
Elvic	Poly(vinyl chloride)	Solvay
Evenglo	Polystyrene	Sinclair-Koppers Co., Inc.
Exon	Poly(vinyl chloride)	Firestone Plastics
Flovic	Poly(vinyl acetate)	Imperial Chemical Industries, Ltd.
Fluorel	Poly(vinylidene fluoride)	Minnesota Mining and Mfg. Co.
Foamex	Poly(vinyl formal)	General Electric Co.
Formex	Poly(vinyl acetal)	General Electric Co.
Formvar	Poly(vinyl formal)	Shawinigan Resins Corp.
Fostacryl	Poly(styrene-co-acrylonitrile)	Foster Grant Co.
Fostalene	Plastic	Foster Grant Co.
Fostarene	Polystyrene	Foster Grant Co.
FPC	PVC resins compound	Firestone Tire & Rubber Co.
Gelvatex	Poly(vinyl acetate) emulsions	Shawinigan Resins Corp.
Gelvatol	Poly(vinyl alcohol)	Shawinigan Resins Corp.
Geon	Poly(vinyl chloride)	B. F. Goodrich Chemical Co.
Heveaplus	Copolymer of methyl methacrylate and rubber	Generic name
Hi-Blen	ABS polymers	Japanese Geon Co.
Hostyren	Polystyrene	Hoechst
Hycar	Butadiene acrylonitrile copolymer	B. F. Goodrich Chemical Co.

Table H Continued

Trade or brand name	Product	Manufacturer
Implex	Acrylic resins	Rohm & Hass Co.
Kralac	ABS resins	Uniroyal, Inc.
Kralastic	ABS	Uniroyal, Inc.
Koroseal	Poly(vinyl chloride)	B. F. Goodrich Chemical Co.
Kralon	High-impact styrene and ABS resins	Uniroyal, Inc.
Krene	Plasticized vinyl film	Union Carbide Corp.
K-Resin	Butadiene-styrene copolymer	Phillips Petroleum Co.
Kurlon	Poly(vinyl alcohol) fibers	
Kydex	Acrylic-poly(vinyl chloride) sheet	Rohm & Haas Co.
Kynar	Poly(vinylidene fluoride)	Pennwalt Chemicals Corp.
Lemac	Poly(vinyl acetate)	Borden Chemical Co.
Lemol	Poly(vinyl alcohol)	Borden Chemical Co.
Levapren	Ethylene-vinylacetate copolymers	Farbenfabriken Bayer AG
Lucite	Poly(methyl methacrylate) and copolymers	E. I. du Pont de Nemours & Co., Inc.
Lustrex	Polystyrene	Monsanto Chemical Co.
Lutonal	Poly(vinyl ethers)	Badische Anilin & Soda-Fabrik AG
Lutrex	Poly(vinyl acetate)	Foster Grant Co.
Luvican	Poly(vinyl carbazole)	Badische Anilin & Soda-Fabrik AG
Marvinol	Poly(vinyl chloride)	Uniroyal, Inc.
Mipolam	Poly(vinyl chloride)	Dynamit Nobel
Mowilith	Poly(vinyl acetate)	Farbwerke Hoechst AG
Mowtol	Poly(vinyl alcohol)	Farbwerke Hoechst AG
Mowital	Poly(vinyl butyral)	Farbwerke Hoechst AG
Nalgon	Plasticized poly(vinyl chloride)	Nalge Co.
Nipeon	Poly(vinyl chloride)	Japanese Geon Co.
Nipoflex	Ethylene-vinyl acetate copolymer	Toyo Soda Mfg. Co.
Noan	Styrene-methyl methacrylate copolymer	Richardson Corp.
Novodur	ABS polymers	Farbenfabriken Bayer AG
Opalon	Poly(vinyl chloride)	Monsanto Chemical Co.
Oppanol C	Poly(vinyl isobutylether)	Badische Anilin & Soda-Fabrik AG
Orlon	Acrylic fiber	E. I. du Pont de Nemours & Co., Inc.
Paracryl	Butadiene-acrylonitrile copolymer	U.S. Rubber Co.
Pee Vee Cee	Rigid poly(vinyl chloride)	ESB Corp.

Table H Continued

Trade or brand name	Product	Manufacturer
Pelaspán	Expandable polystyrene	Dow Chemical Co.
Perspex	Acrylic resins	Imperial Chemical Industries Ltd.
Pevalon	Poly(vinyl alcohol)	May and Baker Ltd.
Philprene	Styrene–butadiene rubber	Phillips Petroleum Co.
Plexiglas	Acrylic sheets	Rohm & Haas Co.
Plexigum	Acrylate and methacrylate resins	Rohm & Haas Co.
Plioflex	Poly(vinyl chloride)	Goodyear Tire & Rubber Co.
Pliovic	Poly(vinyl chloride)	Goodyear Tire & Rubber Co.
Polysizer	Poly(vinyl alcohol)	Showa Highpolymer Co.
Polyviol	Poly(vinyl alcohol)	Wacker Chemie GmbH
Ravinil	Poly(vinyl chloride)	ANIC, S.P.A.
Resistoflex	Poly(vinyl alcohol)	Resistoflex Corp.
Restiroló	Polystyrene	Societa Italiana Resine
Rhoplex	Acrylic emulsions	Rohm & Haas Co.
Rucon	Poly(vinyl chloride)	Hooker Chemical Corp.
Saflex	Poly(vinyl butyral)	Monsanto Co.
Saran	Poly(vinylidene chloride)	Dow Chemical Co.
Solvar	Poly(vinyl acetate)	Shawinigan Resins Corp.
Solvic	Poly(vinyl chloride)	Solvay & Cie
S-polymers	Butadiene–styrene copolymer	Esso Labs
Staflax	Vinyl plasticizers	Reichhold Chemical, Inc.
Starex	Poly(vinyl acetate)	International Latex & Chemical Corp.
Stymer	Styrene copolymer	Monsanto Co.
Styrocel	Polystyrene (expandable)	Styrene Products Ltd.
Styrofoam	Extruded expanded polystyrene; foam	Dow Chemical Co.
Styron	Polystyrene	Dow Chemical Co.
Sullvac	Acrylonitrile–butadiene–styrene copolymer	O’Sullivan Rubber Corp.
Tedlar	Poly(vinyl fluorocarbon) resins	E. I. du Pont de Nemours & Co., Inc.
Terluran	ABS polymers	Badische Anilin & Soda-Fabrik AG
Texicote	Poly(vinyl acetate)	Scott Bader Co.
Trosiplast	Poly(vinyl chloride)	Dynamit Nobel AG
Trulon	Poly(vinyl chloride) resin	Olin Corp.
Tybrene	ABS polymers	Dow Chemical Co.
Tygon	Vinyl copolymer	U.S. Stoneware Co.
Tytil	Styrene–acrylonitrile copolymer	Dow Chemical Co.

Table H Continued

Trade or brand name	Product	Manufacturer
Ultron	Vinyl film	Monsanto Co.
Ultryl	Poly(vinyl chloride)	Phillips Petroleum Co.
Uscolite	ABS copolymer	U.S. Rubber Co.
Vestolit	Poly(vinyl chloride)	Chemische Werke Huls AG
Vestyron	Polystyrene	Chemische Werke Huls AG
Viclan	Poly(vinylidene chloride)	Imperial Chemical Industries, Inc.
Vinac	Poly(vinyl acetate) emulsions	Air Reduction Co.
Vinapas	Poly(vinyl acetate)	Wacker Chemie GmbH
Vinidur	Poly(vinyl chloride)	BASF Corp.
Vinoflex	Poly(vinyl chloride)	BASF Corp.
Vinol	Poly(vinyl alcohol)	Air Reduction Co.
Vynylite	Poly(vinyl chloride-co-vinyl acetate)	Union Carbide Corp.
Vinyon	Poly(vinyl chloride-co-acrylonitrile)	Union Carbide Corp.
Vipla	Poly(vinyl chloride)	Montecatini Edison, S.p.A.
Vybak	Poly(vinyl chloride)	Bakelite Xylonite Ltd.
Vygen	Poly(vinyl chloride)	General Tire & Rubber Co.
Vynex	Rigid vinyl sheeting	Nixon-Baldwin Chemicals, Inc.
Vyram	Rigid poly(vinyl chloride)	Monsanto Co.
Welvic	Poly(vinyl chloride)	Imperial Chemical Industries, Inc.

Source: Portions of the data were compiled from R. B. Seymour and C. E. Carraher, Jr., *Polymer Chemistry*, Marcel Dekker Inc., New York (1992).

Table I Industrially Important Additional Polymers

Name	Repeating unit	Typical properties	Typical uses
Polyacrylonitrile (including acrylic fibers)	$\begin{array}{c} \text{H} & \text{H} \\ & \\ -(\text{C}-\text{C})- \\ & \\ \text{H} & \text{CN} \end{array}$	High strength; good stiffness; tough; abrasion resistant; resilient; good flex life; relatively good resistance to moisture and stains, chemicals, insects, and fungi; good weatherability	Carpeting, sweaters, skirts, socks, slacks, baby garments
Poly(vinyl acetate)	$\begin{array}{c} \text{H} & & \text{H} \\ & & \\ -(\text{C}-\text{C})- & \text{O}-\text{C}-\text{CH}_3 \\ & // & \\ \text{H} & \text{O} & \end{array}$	Water sensitive with respect to physical properties such as adhesion and strength; generally good weatherability, fair adhesion	Lower molecular weight used in chewing gum, intermediate in production of poly(vinyl alcohol), water-based emulsion paints
Poly(vinyl alcohol)	$\begin{array}{c} \text{H} & \text{H} \\ & \\ -(\text{C}-\text{C})- & \text{O}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$	Water soluble, unstable in acidic or basic aqueous systems; fair adhesion	Thickening agent for various suspension and emulsion systems, packaging film, wet-strength adhesive
Poly(vinyl butyral)	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ -(\text{C}-\text{C}-\text{C})- & \text{O}-\text{C}-\text{CH}_2\text{CH}_2\text{CH}_3 \\ & & \\ \text{H} & \text{H} & \text{H} \end{array}$	Good adhesion to glass; tough; good stability to sunlight; good clarity; insensitive to moisture	Automotive safety glass as the interlayer
Poly(vinyl chloride) and poly(vinylidene chloride) (called "the vinyls" or "vinyl resins")	$\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ -(\text{C}-\text{C})- & \text{Cl} & -(\text{C}-\text{C})- & \text{Cl} \\ & & & \\ \text{H} & \text{Cl} & \text{H} & \text{Cl} \end{array}$	Relatively unstable to heat and light, fire resistant; resistant to chemicals, insects, fungi; resistant to moisture	Calendered products such as film sheets and floor coverings; shower curtains, food covers, rainwear, handbags, coated fabrics, insulation for electrical cable and wire, phonograph records

Polytetrafluoroethylene
(Teflon)



Insoluble in most solvents;
chemically inert; low dielectric
loss; high dielectric strength;
uniquely nonadhesive; low
friction properties; constant
electrical and mechanical
properties from 20°C to about
250°C; high impact strength; not
hard; outstanding mechanical
properties

Coatings for frying pans, etc.;
wire and cable insulation;
insulation for motors, oils,
transformers, generators;
gaskets; pump and valve
packings; nonlubricated
bearings

Polyethylene (low-density,
branched)



Dependent on molecular weight,
branching; molecular-weight
distribution, etc.; good toughness
and pliability over a wide
temperature range; outstanding
electrical properties; good
transparency in thin films; inert
chemically; resistant to acids and
bases; ages on exposure to light
and oxygen; low density; flexible
without plasticizer; resilient; high
tensile strength; moisture resistant

Films; sheeting used in bags,
pouches, produce wrapping,
textile materials, frozen foods,
etc.; drapes, table cloths;
covers for construction, ponds,
greenhouses, trash can liners,
etc.; electrical wire and cable
insulator; coating of foils,
papers, other films; squeeze
bottles


Polyethylene (high-density,
linear)

Most of the differences in
properties between branched and
linear concerns the high
crystallinity of the latter; linear
polyethylene has a high T_g , T_m ,
softening range, greater hardness
and tensile strength

Bottles, housewares, toys, films,
sheets, extrusion coating,
pipes, conduit, wire and cable
insulation

Table I Continued

Name	Repeating unit	Typical properties	Typical uses
Polypropylene	$\begin{array}{c} \text{H} & \text{H} \\ & \\ (-\text{C}-\text{C}-) \\ & \\ \text{H} & \text{CH}_3 \end{array}$	Lightest major plastic; its high crystallinity imparts to it high tensile strength, stiffness, and hardness, good gloss, high resistance to marring; high softening range permits polymer to be sterilized; good electrical properties, chemical inertness, moisture resistance	Filament—rope, webbing, cordage; carpeting; injection-molding applications in appliance, small houseware, and automotive fields
Polyisoprene (<i>cis</i> -1,4-polyisoprene)	$\begin{array}{c} & & \text{C}=\text{C} \\ & \diagdown & / \\ (-\text{C} & - & \text{C}-) \\ / & \backslash & \\ \text{H} & \text{H} & \text{H} \end{array}$	Structure closely resembling that of natural rubber; properties similar to those of natural rubber	Replacement of natural rubber; often preferred because of its greater uniformity and cleanliness
SBR (styrene-butadiene rubber)	Random copolymer	Generally slightly poorer physical properties than those of natural rubber	Tire treads for cars, inferior to natural rubber with respect to heat buildup and resilience, thus not used for truck tires; belting; molded goods, gum, flooring, rubber shoe soles, electrical insulation, hoses
Butyl rubber (copolymer of isobutylene with small amounts of isoprene added to permit vulcanization)	Amorphous, isoprene—largely 1,4 isomer	Good chemical inertness; low gas permeability; high viscoelastic response to stresses; less sensitive to oxidative aging than most other elastomers; better ozone resistance than natural rubber; good solvent resistance	About 70–60% used for inner tubes for tires

Polychloroprene (Neoprene)	Mostly 1,4 isomer	Outstanding oil and chemical resistance; high tensile strength, outstanding resistance to oxidative degradation and aging; good ozone and weathering resistance; dynamic properties are equal to or greater than those of most synthetic rubber and only slightly inferior to those of natural rubber	Can replace natural rubber in most applications; gloves, coated fabrics, cable and wire coatings, hoses, belts, shoe heels, solid tires
Polystyrene	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} - \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$ 	Clear; easily colored; easily fabricated; transparent; fair mechanical and thermal properties; good resistance to acids, bases, oxidizing, and reducing agents; readily attacked by many organic solvents; good electrical insulator	Used for the production of ion-exchange resins, heat- and impact-resistant copolymers, ABS resins, etc., foams, plastic optical components, lighting fixtures, housewares, toys, packaging, appliances, home furnishings
Poly(methyl methacrylate)	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} - \text{C} \\ & / & \diagdown \\ \text{H} & & \text{C} = \text{O} \\ & & \\ & & \text{O} \\ & & \\ & & \text{CH}_3 \end{array}$	Clear, transparent, colorless; good weatherability; good impact strength; resistant to dilute basic and acidic solutions; easily colored; good mechanical and thermal properties; good fabricability; poor abrasion resistance compared to glass	Available in cast sheets, rods, tubes, and molding and extrusion compositions, applications where light transmission is needed, such as tail- and signal-light lenses, dials, medallions, brush backs, jewelry, signs, lenses, skylight "glass,"

Source: Portions of the data were compiled from R. B. Seymour and C. E. Carraher, Jr., *Polymer Chemistry*, Marcel Dekker, Inc., New York (1992).

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